Sc Lib.

MAR 17 1949

REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXIX] *SECTION A* [No. 1

JANUARY, 1949

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

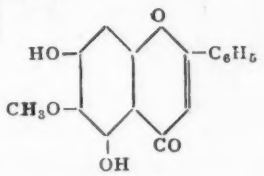
Part XVII. A Synthesis of Oroxylin-A

By V. V. Sreerama Murti and T. R. Seshadri

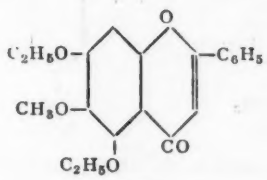
(From the Department of Chemistry, Andhra University, Waltair)

Received October 5, 1948

The isolation of Oroxylin-A in a pure condition was recently reported.[1] In the same communication its constitution (I) was established by preparing its diethyl ether and showing that it is identical with a synthetic sample of 5:7-diethoxy-6-methoxy flavone (II). Oroxylin-A itself has now been synthesised and the experiments carried out in this connection are described in this paper.

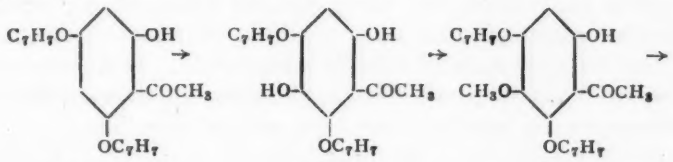


(I)

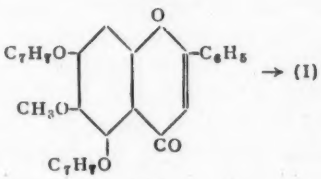


(II)

The general method adopted is that of baicalein and scutellarein synthesis of Sastri and Seshadri[2] in which the nuclear oxidation of a phloroacetophenone derivative is an essential stage. A simple scheme explored first was as follows:—



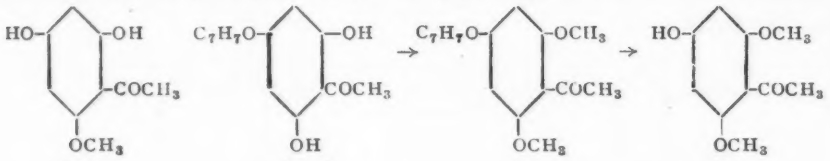
(III) (IV) (V)



(VI)

The benzylation of phloroacetophenone was earlier reported[3] to yield a nuclear benzylated product. By employing suitable conditions it has now been possible to make the dibenzyl ether (III). Its constitution has been established by methylation with excess of dimethyl sulphate and subsequent debenzylation whereby 2:4-dihydroxy-6-methoxy acetophenone (VII)[4] is obtained. But so far experiments to oxidise this dibenzyl ether have not been successful.

In the search for a better starting material mono-benzylation of phloroacetophenone has next been attempted. Employing a little over one mole of benzylchloride a mono-benzyl ether could be obtained fairly readily. It is a pure individual with a sharp melting point and on examination has proved to be the 4-benzyl ether (VIII). Its constitution has been established by carrying out complete methylation (IX) followed by debenzylation whereby 2:6-dimethoxy-4-hydroxy-acetophenone (X)[5] is obtained.

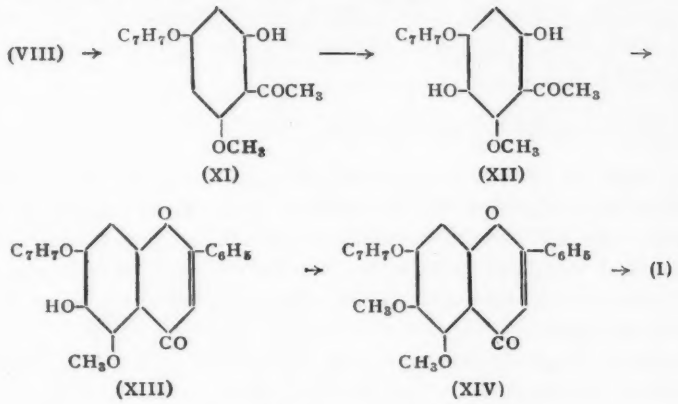


(VII) (VIII) (IX) (X)

The course of the mono-benzylation of phloroacetophenone follows that of partial benzoylation and methylation so far recorded. By the benzoylation of phloroacetophenone and phloropropiophenone Canter, Curd and Robertson[5] obtained mainly the *p*-monobenzoates and only in small amounts the isomeric orthobenzoates. Earlier Karrer[6] employed phlorobutyrophenone and phlorobenzophenone and obtained only the corresponding para benzoates. More recently Kuhn, *et al.*,[7] methylated *ω*-methoxy-phloroacetophenone using restricted quantities of diazomethane and obtained only the *p*-methyl ether in a poor yield. As Robertson, *et al.*, have remarked it is quite possible that in all these cases traces of the isomeric ortho-compounds are produced but have escaped detection.

Partial methylation with dimethyl sulphate of the mono-benzyl ether (VIII) has yielded 4–O-benzyl-6-O-methyl-phloroacetophenone (XI). This can be debenzylated to the monomethyl-phloroacetophenone (VII). The reverse of this process, that is the benzylation of 2-methyl-phloroacetophenone has been reported by Gulati and Venkataraman.[4] The product obtained by their method is identical with the one made from (VIII). Oxidation of (XI) proceeds satisfactorily forming the quinol ketone (XII). During the subsequent Allan-Robinson condensation using this quinol

ketone (XII) and benzoic anhydride and sodium benzoate partial demethylation in the 5-position of the flavone seems to take place, because the product gives a prominent ferric reaction. Hence the stage (XIII) has not been definitely characterised. On methylation, however, the dimethyl-monobenzyl ether of baicalein (XIV) can be obtained pure. By the action of hydrobromic acid in acetic acid on this substance debenzylation and partial demethylation in the 5-position take place yielding oroxylin-A (6-O-methyl baicalein) (I). The suitability of this reagent for the removal of the 5-methoxyl has been shown by the earlier work of Shah, Virkar and Venkataraman and Seshadri and Venkateswarlu using calycopterin methyl ethers.[8] In the present case oroxylin-A is obtained pure and the synthetic sample agrees in every respect with the natural sample described recently.[1] For confirming the identity the diacetate and diethyl ether have also been prepared and compared with the natural samples.



Experimental

4-*O*-*Benzyl-phloracetophenone* (*VIII*)

Dry phloracetophenone (2 g.) was dissolved in anhydrous acetone (25 c.c.) and to the solution were added redistilled benzyl chloride (1·0 c.c.) and freshly ignited potassium carbonate (10 g.). The mixture was refluxed on a water-bath for 3 hours with occasional shaking. The red solution was filtered, the solvent distilled off and the benzyl chloride removed by passing steam. The red oily product solidified on cooling and was purified by recrystallisation from a large quantity of alcohol. The monobenzyl ether was thus obtained as cream-coloured prisms melting with decomposition at 188–9°. Yield, 0·4 g.

The compound was sparingly soluble in alcohol but dissolved readily in acetone. It dissolved in aqueous sodium hydroxide to give a pale yellow solution and was reprecipitated by the addition of acid. In alcoholic solution, it gave a brown colour with ferric chloride. Unlike the dimethyl and the dibenzyl ethers of phloracetophenone, the monobenzyl ether did not give any colour with concentrated nitric acid. (Found: C, 69·5; H, 5·7; $C_{15}H_{14}O_4$ requires C, 69·8 and H, 5·4%).

The above mono-benzyl ether (0·5 g.) was methylated using excess of dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.) in dry acetone medium (20 c.c.) by boiling for 20 hours. The product did not solidify even on keeping in the refrigerator for several days. So it was debenzylated by heating with concentrated hydrochloric acid (5 c.c.) in glacial acetic acid solution (10 c.c.). The mixture was diluted with water and extracted with ether. On evaporating the ether and then removing the benzyl chloride in steam, 2:6-dimethyl phloracetophenone (X) separated out. It crystallised from dilute alcohol as colourless rectangular rods and melted at 183–4°.

4-O-Benzyl-6-O-methyl-phloracetophenone (XI)

To a solution of the mono-benzyl ether (1·3 g.) in dry acetone (50 c.c.) were added freshly distilled dimethyl sulphate (0·5 c.c.) and ignited potassium carbonate (5 g.) and the mixture was gently refluxed on a water-bath for 6 hours. The inorganic salts were then filtered and washed with warm acetone; the filtrate was concentrated and the residue treated with water when the benzyl-methyl ether separated as an oil which completely solidified on keeping in the refrigerator. It was crystallised once from alcohol and then from acetone-petroleum ether mixture when it was obtained as colourless flat needles melting at 73–4°. Yield 1·0 g. The compound was soluble with difficulty in sodium hydroxide solution, sparingly soluble in alcohol and easily in acetone. It gave a pinkish brown colour with ferric chloride in alcohilic solution and turned blue with concentrated nitric acid. (Found: C, 70·2; H, 6·2; $C_{16}H_{16}O_4$ requires C, 70·6 and H, 5·9%).

On debenzylation with concentrated hydrochloric acid in glacial acetic solution, 2-methyl phloracetophenone was obtained, mp. 203–4°, which did not depress the melting of an authentic specimen. Further the benzyl-methyl ether was identical with the sample obtained by the benzylation of 2-O-methyl-phloracetophenone according to the procedure of Gulati and Venkataraman.[4]

2: 5-*Dihydroxy*-4-*benzyloxy*-6-*methoxy-acetophenone* (*XII*)

2-Hydroxy-4-benzyloxy-6-methoxy acetophenone (XI; 13·0 g.) was dissolved in pyridine (15 c.c.) and aqueous sodium hydroxide (20 g. in 150 c.c. of water) added. To the continuously stirred mixture was let in a solution of potassium persulphate (15 g. in 350 c.c. of water) dropwise during the course of 4 hours, the flask being kept at a temperature of 15–20°. The stirring was continued for a further period of 2 hours and the deep red solution allowed to stand for 24 hours. The reaction mixture was then rendered acid to congo-red by addition of hydrochloric acid, the precipitated unchanged ketone (6·0 g.) filtered off, and the aqueous filtrate was extracted once with ether to remove the last traces. It was then treated with sodium sulphite (5 g.), concentrated hydrochloric acid (50 c.c.) and benzene (100 c.c.) and the mixture heated in a boiling water-bath for half-an-hour. The reaction mixture was cooled, the benzene layer separated and the aqueous solution repeatedly extracted with ether. The total benzene and ether extracts were dried over anhydrous sodium sulphate and the solvents distilled off, the last 100 c.c. being removed under reduced pressure. The dihydroxy compound was obtained as a yellow oil which solidified on cooling and scratching with a glass-rod. It was crystallised from dilute alcohol when it was obtained as stout yellow prisms melting at 161–2°. Yield, 1·7 g. The yield and purity of the compound were found to suffer considerably on longer heating for hydrolysis or evaporating the extracts with exposure to air.

The compound was moderately soluble in hot water, readily in alcohol and acetone, but sparingly in light petroleum. Its solution in aqueous sodium hydroxide was yellow in the beginning and turned reddish brown on standing. In alcoholic solution it gave a transient green colouration with ferric chloride which rapidly turned brown. (Found: C, 67·1; H, 5·8; $C_{16}H_{16}O_5$ requires C, 66·8 and H, 5·6%).

Allan-Robinson condensation

The dihydroxy ketone obtained above (2·9 g.) was intimately mixed with benzoic anhydride (13·6 g.) and sodium benzoate (5·7 g.) and the mixture was heated *in vacuo* for 4 hours. The cake was broken up, suspended in alcohol and refluxed for half-an-hour on a water-bath after the addition of aqueous sodium hydroxide (5 g. in 10 c.c. of water). The alcohol was removed under reduced pressure, the residue dissolved in water, the dark-brown solution filtered and saturated with carbon dioxide. It was extracted with ether, the ether extract dried over anhydrous sodium sulphate

and the solvent removed. An yellow oil was obtained which turned into a solid on rubbing with a glass rod. To hydrolyse any 3-benzoyl compound that might have been formed, the solid was refluxed with 5% aqueous sodium carbonate (20 c.c.) for one hour. The yellow solution was filtered and acidified when the product was precipitated as a yellowish-brown solid. It could be crystallised from rectified spirit. But it gave a deep greenish-brown colour with ferric chloride in alcoholic solution and did not have a sharp melting point. It, therefore, appeared to be a mixture of the 6-hydroxy and 5:6-dihydroxy (partially demethylated) compounds and hence was directly used for methylation after thorough drying.

5:6-*Dimethoxy-7-benzyloxy-flavone* (*XIV*)

The above mixture (0·5 g.) was refluxed in dry acetone (25 c.c.) solution with ignited potassium carbonate (5 g.) and freshly distilled dimethyl sulphate (0·5 c.c.) for a period of 30 hours. The acetone solution was filtered and the potassium salts washed with a small quantity of hot acetone. On distilling off the solvent from the filtrate, a pale yellow, viscous oil was obtained which solidified on leaving in the ice-chest for a few days. The product crystallised from absolute alcohol as colourless plates melting at 168–9°. It did not dissolve in aqueous sodium hydroxide and did not give colour with ferric chloride. (Found: C, 73·9; H, 4·9; $C_{24}H_{20}O_5$ requires C, 74·2 and H, 5·2%).

5:7-*Dihydroxy-6-methoxy-flavone*: *Oroxylin-A* (*I*)

5:6-Dimethoxy-7-benzyloxy flavone **XIV** (0·5 g.) was dissolved in glacial acetic acid (10 c.c.), hydrobromic acid in glacial acetic acid solution (10 c.c.) added and the mixture heated at 60° for one hour. The solution was cooled, diluted with water and extracted with ether and the solvent removed from the extract. After distilling off the benzyl bromide in steam, an yellow oil was left behind. It solidified on leaving in the ice-chest overnight and rubbing with a glass rod. The compound crystallised from alcohol as pale yellow plates and prisms melting at 219–20°; the mixed melting point with a pure natural sample of Oroxylin-A was undepressed. It was identical in all its properties and colour reactions with the natural sample. (Found: OMe, 10·7%; $C_{16}H_{12}O_5$ requires OCH_3, 10·9%).

For further confirmation, the acetate and the ethyl ethers were also prepared using the synthetic specimen. They were identical with the natural samples and the mixed melting points were undepressed,

[WITH K. VENKATESWARA RAO]

2-Hydroxy-4: 6-dibenzyloxy-acetophenone (III)

Phloracetophenone (2·5 g.) which had been previously dried in an air oven at 120° for two hours, was dissolved in dry acetone (80 c.c.) and freshly ignited potassium carbonate (8 g.) and benzyl chloride (4·2 c.c.) were added and the mixture refluxed for 20 hours on a water-bath with occasional shaking. At the end of this period, acetone was distilled off and water added to dissolve the inorganic salts. The solution was steam-distilled to remove traces of benzyl chloride. The remaining oil was extracted with ether, washed with very dilute aqueous sodium hydroxide and then with water. The solid obtained by evaporating the ether solution was crystallised from methyl alcohol when 2-hydroxy-4: 6-dibenzyloxy-acetophenone separated out as colourless rectangular rods melting at 98–100°. Yield, 1·5 g.

It was soluble in acetone, alcohol and petroleum ether. Like the corresponding dimethyl ether of phloracetophenone, it was sparingly soluble in aqueous alkali. It gave an intense reddish-brown colour with alcoholic ferric chloride and a deep blue colour with conc. nitric acid. (Found: C, 75·7; H, 5·4; $C_{22}H_{20}O_4$ requires C, 75·9 and H, 5·7%.)

The above dibenzyl ether (1 g.) was methylated using acetone (50 c.c.), dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (5 g.) and boiling for 15 hours. The inorganic salts were filtered off and washed with warm acetone. The acetone filtrate was evaporated and the residue taken up in ether and washed with aqueous sodium hydroxide and water. On evaporating the ether solution a reddish brown oil was obtained which was directly subjected to debenzylation using glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (4 c.c.) and heating on a boiling water-bath for one hour. Excess of water was added and the oily product ether-extracted. The ether solution was shaken with aqueous bicarbonate to remove the acetic acid and subsequently with 1% aqueous sodium hydroxide. On acidifying the alkaline solution, a semi-solid product was obtained. It crystallised from benzene as cream-coloured prisms melting at 203–4° alone or in admixture with an authentic sample of 2-methyl phloracetophenone.

SUMMARY

Phloroacetophenone-2: 4-dibenzyl ether is prepared; it does not undergo persulphate oxidation satisfactorily. Monobenzylation of phloroacetophenone yields the 4-benzyl ether readily; it is partially methylated to the 2-methyl-4-benzyl ether. Starting with this compound, persulphate oxidation, Allan-Robinson condensation using benzoic anhydride and sodium

benzoate and methylation produce 5:6-dimethoxy-7-benzyloxyflavone. Hydrobromic acid causes besides debenzylation, demethylation in the 5-position. The final product is the 6-methyl ether of baicalein which is identical with oroxylin-A isolated from the root and stem barks of *Oroxylum indicum*.

References

1. Row, Sastri, Seshadri and Thiruvengadam .. *Proc. Ind. Acad. Sci.*, A, 1948, **28**, 189.
2. Sastri and Seshadri .. *Ibid.*, 1946, **23**, 262 and 273.
3. Gulati, Seth and Venkataraman .. *J. C. S.*, 1934, 1765.
4. Sonn and Bulow .. *Ber.*, 1945, **58**, 1691.
   Gulati and Venkataraman .. *J. C. S.*, 1936, 267.
5. Canter, Curd and Robertson .. *Ibid.*, 1931, 1245.
6. Karrer .. *Helv., Chim. Acta.*, 1919, **2**, 466.
7. Kuhn, *et al.* .. *Ber.*, 1944, 202, *C. A.*, 1945, 3285.
8. Shah, Virkar and Venkataraman .. *J. I. C. S.*, 1942, **19**, 135.
   Seshadri and Venkateswarlu .. *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 349

SYNTHESIS OF SOME IMPORTANT PARTIAL METHYL ETHERS OF FLAVONOLS

By S. Rajagopalan, P. Ramachandra Rao, K. Visweswara Rao and T. R. Seshadri

(From the Department of Chemistry, Andhra University, Waltair)

Received October 5, 1948

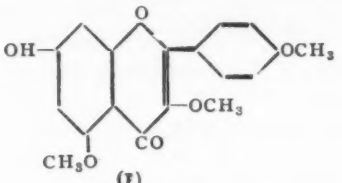
The most satisfactory method of locating the position of the sugar unit in the anthoxanthin glycosides is to carry out complete methylation and subsequently hydrolyse the product. The location of the hydroxyl group in the partial methyl ether thus produced will then settle the position of the sugar residue. The chief difficulties in the study of these partial methyl ethers are two: (1) they do not undergo fission with alkali satisfactorily; (2) except in a few favourable cases their synthesis is difficult. These difficulties can be overcome by employing the technique of ethylation and examining the mixed ethers of flavones thus produced. This procedure has been satisfactorily adopted in the case of gossypin,[1] hibiscitrin,[2] quercimeritrin and quercetagitrin[3] and populnin.[4] The synthesis of the partial methyl ethers themselves in some of the more difficult cases has now been accomplished with the help of partial benzylation. The method is capable of extension to the preparation of analogous compounds.

3 : 5 : 4′ : *O-Trimethyl-kæmpferol*

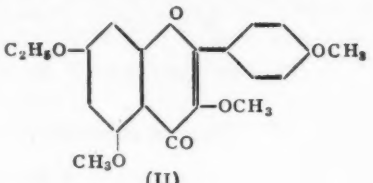
Populnin when methylated and hydrolysed yields a monohydroxy compound melting at 284–85°. Its constitution was determined by comparing it with all the known trimethyl ethers of kæmpferol having a free hydroxyl group in the 3, 5 and 4′ positions. Since it was different from these it was considered to be the 7-hydroxy isomer having the constitution (I). Conclusive evidence[4] was provided by the unambiguous synthesis of its ethyl derivative (II) and also of the fission ketone (III).

The above trimethyl ether of kæmpferol (7-hydroxy compound) was reported to have been obtained in the degradation of robinin and its properties as recorded by Zemplen and Bognar[5] agree with those of the partial methyl ether derived from populnin. The same compound was described by Nakamura and Hukuti[6] in connection with their study of equisetrin which is considered to be kæmpferol-7-diglucoside. The last mentioned authors described also its synthesis starting from the monomethyl ether of phloroglucinol which was first condensed with methoxy-acetonitrile (Hoesch

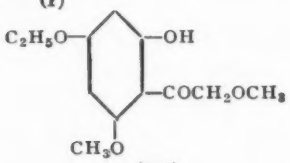
reaction). The resulting ketone (IV) was then subjected to the Allan-Robinson condensation with the anhydride and sodium salt of anisic acid.



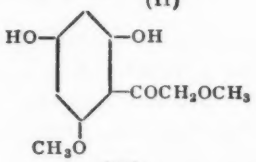
(I)



(II)



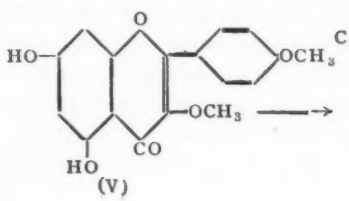
(III)



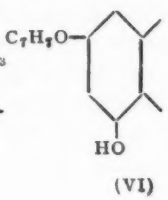
(IV)

In regard to this synthesis the preparation of the monomethyl ether of phloroglucinol in a pure state is time consuming. Further there is the possibility of demethylation occurring in the 5-position during the Allan-Robinson condensation.[7] Remethylation of this position without affecting others is not possible. In this connection it may be mentioned that Nakamura and Hukuti[6] recorded the melting point of the acetate of their synthetic product as 203° which is too high. A simpler synthesis of this reference compound which is free from defects should therefore be considered necessary. This has now been achieved by employing the technique of partial benzylation. The feasibility of this method in the flavone series was shown earlier in connection with the synthesis of wogonin.[8]

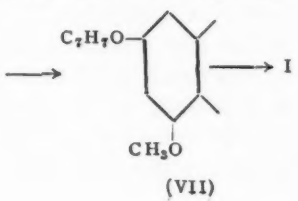
5 : 7-Dihydroxy-3 : 4′-dimethoxy flavone (V) has been recently subjected to partial benzylation using the requisite amount of benzyl chloride.[9] The reaction takes place in the 7-position leaving the resistant 5-hydroxyl free and the properties of the product agree with the requirements of the structure (VI). Subsequent methylation with excess of dimethyl sulphate and final debenzylation of (VII) using a mixture of concentrated hydrochloric acid and glacial acetic acid yield the 7-hydroxy-3 : 5 : 4′-trimethoxy flavone (I). This is found to be identical with the degradation product from populnin.



(V)



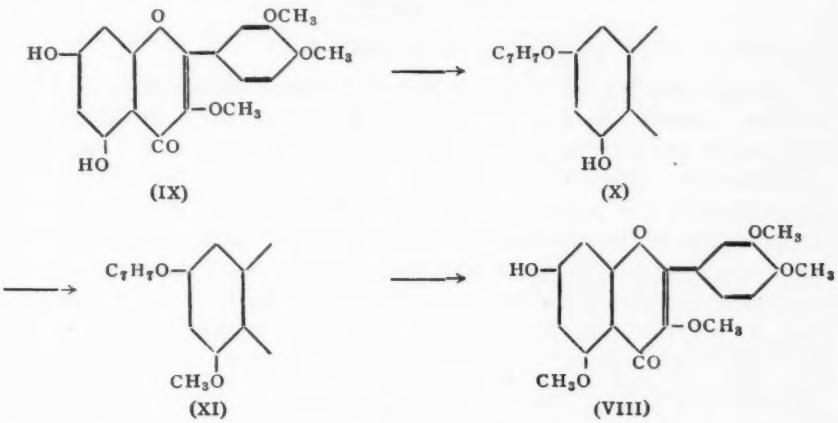
(VI)



(VII)

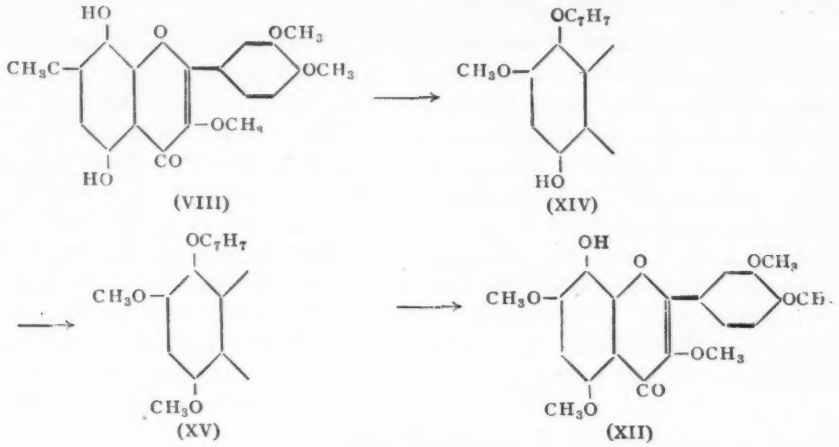
3:5:3′:4′-*O-Tetramethyl quercetin*

In an earlier paper[3] it was pointed out that the constitution of quercetin tetramethyl ether (VIII) obtained by the hydrolysis of methyl quercimeritrin was originally arrived at by Attree and Perkin[10] by eliminating other possibilities but no synthetic support was given. This was provided in that paper by ethylating the hydroxy compound (VIII) and showing that it is identical with 7-ethoxy-3:5:3′:4′-tetramethoxy flavone prepared synthetically. Following the same lines as given above for the partial methyl ether of kæmpferol and using the technique of partial benzylation the required quercetin tetramethyl ether has now been made, the starting point being 5:7-dihydroxy-3:3′:4′-trimethoxy flavone[11] (IX). The final product is found to be identical with the tetramethyl ether obtained from quercimeritrin by methylation and hydrolysis. For purposes of comparison the melting point of the hydroxy compound, its reactions with alkali and ferric chloride and the melting point of the acetate are used.



3:5:7:3′:4′-*O-Pentamethyl-gossypetin*

The third compound that has now been synthesised by this method is the pentamethyl ether of gossypetin (XII) obtained from gossypin. Its constitution was also first settled by the elimination of other possibilities[12] and later by an unambiguous synthesis of its ethyl ether.[1] The synthesis of the hydroxy compound itself starts from the quinol[13] (XIII) prepared by the persulphate oxidation of quercetin-tetramethyl ether and passes through the stages of partial benzylation of the 8-position, methylation and debenzylation as shown below. The synthetic product agrees in every respect with the compound obtained from gossypin.



(VIII) (XIV) (XV) (XII)

Experimental

7-Benzyloxy-3 : 5 : 4′-trimethoxy-flavone (VII)

The preparation of 3 : 4′-dimethoxy-5-hydroxy-7-benzyloxyflavone (VI) has been recently described by Balakrishna and Seshadri.[9] It (0·5 g.) was dissolved in dry acetone (25 c.c.) and anhydrous potassium carbonate (5 g.) and dimethyl sulphate (0·5 c.c.) were added. The mixture was refluxed for 24 hours. The potassium salts were filtered off and washed with hot acetone. The filtrate was concentrated over a water-bath as far as possible and water was added to the residue when a brown solid separated out. It was filtered and crystallised first from alcohol and finally from ethyl acetate when it separated out slowly as colourless short rectangular plates and prisms melting at 118–20° with decomposition. (Found: C, 71·9; H, 5·5; $C_{25}H_{22}O_6$ requires C, 71·8; H, 5·4%.)

7-Hydroxy-3 : 5 : 4′-trimethoxy-flavone (I)

The above 7-benzyloxy compound (VII) (0·3 g.) was dissolved in glacial acetic acid (6 c.c.) and the solution was treated while hot with concentrated hydrochloric acid (4 c.c.). The mixture was kept at the temperature of the boiling water-bath for one hour. It was then diluted with water and set aside. A brown sticky solid separated out. It was filtered and crystallised twice from alcohol when it came out as colourless short needles melting at 283–85°. (Found: C, 66·1; H, 5·2; $C_{18}H_{16}O_6$ requires C, 65·9 and H, 4·9%.) The substance was soluble in alkali to form a light yellow solution and gave no colour with ferric cholride in alcoholic solution. It was only sparingly soluble in alcohol. The mixed melting point with the trimethyl ether

obtained from populnin after methylation and hydrolysis was undepressed. Its acetyl derivative was prepared by boiling with acetic anhydride and a few drops of pyridine. It crystallised from ethyl acetate or acetone in the form of colourless flat needles and narrow rectangular plates melting at 160–62°. Its mixed melting point with the acetate of the trimethyl ether from populnin was undepressed.

7-Benzyloxy-5-hydroxy-3 : 3′ : 4′-trimethoxy flavone (X)

5 : 7-Dihydroxy-3 : 3′ : 4′-trimethoxy flavone[11] (IX) (1·0 g.), dry acetone (30 c.c.), anhydrous potassium carbonate (5·0 g.) and benzyl chloride (0·25 c.c., 1 mol.) were employed and the benzylation carried out as mentioned before. The product was washed with petroleum ether and crystallised from ethyl acetate and petroleum ether mixture. It was obtained as fine yellow needles melting at 131–32°. Yield, 0·6 g. (Found: C, 69·2; H, 5·4; $C_{25}H_{22}O_7$ requires C, 69·1; H, 5·1%.) It was sparingly soluble in aqueous sodium hydroxide and gave a brown colour with alcoholic ferric chloride.

7-Benzyloxy-3 : 5 : 3′ : 4′-tetramethoxy flavone (XI)

The above 5-hydroxy compound (X) (0·5 g.) was methylated using dry acetone (25 c.c.), potassium carbonate (4·0 g.) and dimethyl sulphate (0·5 c.c.). The product crystallised from alcohol as colourless fine needles melting at 171–72°. Yield, 0·4 g. (Found: C, 69·5; H, 5·2; $C_{26}H_{24}O_7$ requires C, 69·6; H, 5·4%.) It was insoluble in aqueous sodium hydroxide and did not give any colour with alcoholic ferric chloride.

7-Hydroxy-3 : 5 : 3′ : 4′-tetramethoxy flavone: Quercetin tetramethyl ether (VIII)

The compound (XI) (0·3 g.) was debenzylated using concentrated hydrochloric acid (4 c.c.) and glacial acetic acid (6 c.c.). The quercetin tetramethyl ether (VIII) crystallised from alcohol acetic acid mixture as colourless rectangular plates melting at 284–85°. (Found: C, 63·7; H, 5·1; $C_{19}H_{18}O_7$ requires C, 63·7; H, 5·0%.) It dissolved in aqueous sodium hydroxide to give a yellow solution and gave no colour with alcoholic ferric chloride. Its acetate crystallised from ethyl acetate as fine colourless needles melting at 174–75°. The above properties are identical with those of the compound obtained from quercimeritrin after methylation and hydrolysis. A mixed melting point of the two samples was undepressed.

8-O-Benzyl-3 : 7 : 3′ : 4′-O-tetramethyl gossypetin (XIV)

A solution of the quinol[13] (XIII) (1·0 g.) in acetone (50 c.c.), benzyl chloride (0·45 c.c.) and anhydrous potassium carbonate (5 g.) were employed.

The crude product was washed well with acidified water and finally with petroleum ether. It crystallised from acetone as lemon yellow needles melting at 159–60°. Yield, 1·1 g. (Found: C, 67·0; H, 5·4; $C_{26}H_{24}O_8$ requires C, 67·3; H, 5·2%.) It was sparingly soluble in alcohol but more easily in acetone and chloroform. It did not dissolve in aqueous sodium hydroxide but the colour of the solid changed to deep yellow on boiling. In alcoholic solution it gave an intense olive green colouration with ferric chloride.

8-O-Benzyl-O-pentamethyl gossypetin (XV)

The above monobenzyl ether (0·8 g.) was boiled with anhydrous acetone (50 c.c.), dimethyl sulphate (1 c.c.) and potassium carbonate (5 g.) for 12 hours. The solid product was washed well with aqueous alkali and subsequently with water. Recrystallisation of it from a mixture of alcohol and acetone yielded colourless long fibrous needles melting at 150–52°. (Found: C, 65·0; H, 5·8; $C_{27}H_{26}O_8$, H_2O requires C, 65·3; H, 5·6%.) Yield, 0·75 g. It was not soluble in alkali and it did not give any colour with alcoholic ferric chloride.

8-Hydroxy-3 : 5 : 7 : 3′ : 4′-pentamethoxy flavone (XII)

The debenzylation of the above compound (XV) (0·5 g.) was effected using glacial acetic acid (15 c.c.) and concentrated hydrochloric acid (3 c.c.). The yellow crystalline product obtained was washed thoroughly with water and then with light petroleum. It crystallised from alcohol as pale yellow rectangular plates melting at 196–98°. It gave a pale brown colour with ferric chloride and in all respects it was identical with the 8-hydroxy compound obtained from gossypin. The mixed melting point was undepressed. Yield, 0·2 g. Its acetate melted at 215–16° and was identical with the acetate of the 8-hydroxy compound obtained from gossypin.

Summary

The following three partial methyl ethers of flavonols which are derivatives of naturally occurring monoglucosides having only one free hydroxyl group have been conveniently synthesised by using the method of partial benzylation: (1) 3 : 5 : 4′-O-trimethyl-kæmpferol derived from populnin and related glycosides, (2) 3 : 5 : 3′ : 4′-O-tetramethyl quercetin derived from quercimeritrin and (3) 3 : 5 : 7 : 3′ : 4′-O-pentamethyl gossypetin derived from gossypin.

REFERENCES

1. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1947, **25**, 397.
2. ———— .. *Ibid.*, 1948, **27**, 209.
3. Rajagopalan and Seshadri .. *Ibid.*, 1948, **28**, 31.
4. Rao and Seshadri .. *Ibid.*, 1946, **24**, 456.
5. Zemplen and Bognar .. *Ber.*, 1941, **74**, 1789.
   .. *B.C.A.*, *A ii*, 1946, 129.
6. Nakamura and Hukuti .. *J. Pharm. Soc. Japan*, 1940, **60**, 449–58.
   .. *B.C.A.*, *A ii*, 1941, 302.
7. Wessely and Moser .. *Monatsh*, 1932, **60**, 26.
   Baker, *et al.* .. *J.C.S.*, 1939, 956.
   Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1945, **22**, 383.
   Seshadri and Venkateswarlu .. *Ibid.*, 1946, **23**, 192.
8. Rao, Rao and Seshadri .. *Ibid.*, 1947, **26**, 13.
9. Balakrishna and Seshadri .. *Ibid.*, 1947, **26**, 217.
10. Attree and Perkin .. *J.C.S.*, 1927, 234.
11. Allan and Robinson .. *Ibid.*, 1926, 2334.
12. Rao and Seshadri .. *Proc. Ind. Acad. Sci.*, **A**, 1946, **24**, 375.
13. ———— .. *Ibid.*, 1947, **25**, 417.

DIFFRACTION OF LIGHT BY SUPERPOSED ULTRASONIC WAVES

By B. Ramachandra Rao

(From the Department of Physics, Andhra University, Waltair)

Received September 7, 1948

(Communicated by Prof. S. Bhagavantam, F.A.SC.)

1. Introduction

The well-known phenomenon of diffraction of light by ultrasonic waves, discovered by Debye and Sears,[1] and Lucas and Biquard,[2] has been satisfactorily explained by Raman and Nath[3] for normal incidence position and at low frequencies. The most important expression giving the diffraction angle is

$$\sin \theta = \pm n\lambda/\lambda^*, \tag{1}$$

where θ is the diffraction angle, n the order of diffraction, λ the wavelength of light in vacuum and λ^* the wavelength of sound in the medium. $J_n^2(v)$ gives the intensity of the nth order spectrum, $J_n(v)$ being the Bessel function of nth order and v being a parameter involving μ, L and λ. They have not, however, studied the nature of diffraction when two or more sound waves are superposed.

The nature of diffraction when two sound waves are present simultaneously in the medium has been experimentally investigated by Bergmann.[4] He found that, when the quartz crystal is excited at two different harmonics n_1 and n_2, spectra corresponding to $n_1 \pm n_2$ were obtained besides those due to frequencies n_1 and n_2. Later Bergmann used two different crystals for generating two incommensurate frequencies of sound waves and by sending light through both the waves, summation and difference lines are obtained as in the previous case. Subsequently Bergmann and Fues[5] have again taken up the investigation and obtained a number of combination lines besides the summation and difference lines. Similar combination lines have been reported by these authors in a glass block which is excited both for the longitudinal and transverse waves. A theoretical interpretation of these observations has been given by Fues.[5] Employing the theories of Raman and Nath and Van Cittart, Fues has deduced expressions for intensities of diffraction spectra obtained when light is sent through a medium in which a number of ultrasonic waves are set up. According to Fues, the angles of diffraction orders is given by

$$\sin \theta = \frac{r\lambda}{\lambda_1^*} + \frac{s\lambda}{\lambda_2^*} + \frac{u\lambda}{\lambda_3^*} + \ldots, \tag{2}$$

where r, s, u, ... are integers, and the intensity of the order is given by

$$\pi J_r^2(v_1)\, J_s^2(v_2)\, J_u^2(v_3) \qquad (3)$$

It is evident from this theory that when two sound waves of frequencies n_1 and n_2 are superposed, diffraction patterns corresponding to $rn_1 \pm sn_2$ will also be obtained and that the intensity of r, sth order is given by $J_r^2(v_1)J_s^2(v_2)$. It also follows that the diffraction pattern will be perfectly symmetrical about the central image. Similar combination spectra have also been reported by Govindarao.[6] Using two different crystals excited by separate oscillators, and immersed in xylol vertically at the two opposite ends of a square glass trough, he has been able to obtain a number of combination lines everyone of which corresponded to one of the values of $rn_1 \pm sn_2$.

With a view to explain the combination lines obtained by Hiedemann and Hosch[7] in solids, Nath[8] has investigated the optical diffraction effects due to two sound waves which pass in the same direction through a glass block. To illustrate the method and justify its applicability, he has first investigated the diffraction of light by two parallel longitudinal sound waves in a liquid. There is next considered the diffraction of light in a glass block due to two parallel sound waves, one of them longitudinal and the other transverse. Results obtained showed the existence of combination lines which are in agreement with the results of Hiedemann and Hosch. Similar results have been obtained by K. Nagabhushana Rao[9] for the intensity of diffraction orders in the case of N systems of sound waves using Raman and Nath's generalised theory.

The theoretical and experimental study of the nature of diffraction has hitherto been confined to superposition of sound waves of two incommensurate frequencies or frequencies in any odd ratio. The special case of superposition of sound waves of frequencies in any even ratio and in definite phase relationship has not been so far studied theoretically or experimentally.

2. Theoretical Investigation by the Author

While studying the variation of intensity of diffraction in different spectra with a view to verify Raman and Nath's theory, the author observed a peculiar feature. There was conspicuous asymmetry in diffraction for normal incidence which was found to be due to the oscillator generating its second harmonic strongly and consequently exciting the crystal at two different frequencies one of which is an octave of the other and also in the same phase. This result led the author to investigate the phenomenon both theoretically and experimentally.

Asymmetry of diffraction of light is a natural consequence of the lack of symmetry in the light wavefront emerging from the medium. By a graphical construction of the resultant wavefront obtained by superposed ultrasonic waves, it is possible to see when asymmetry will be introduced in the diffracted light. Thus, for example, when two sound waves one of which is an octave of the other are superposed in phase, the resultant wavefront will not be symmetrical which consequently leads to asymmetry in the diffraction pattern.

An analytical treatment for the calculation of intensities of diffraction spectra for some special cases of superposed waves is given here using Raman and Nath's simplified theory. The notations employed here are the same as those used in Raman and Nath's earlier publication. Considering at first two sound waves of wavelengths λ^* and $\lambda^*/2$ set up in the medium with a phase difference of Δ so as to produce maximum variations of refractive indices of μ_1 and μ_2 respectively, the refractive index $\mu(x)$ in any layer at a distance x from the origin is given by

$$\mu(x) = \mu_0 + \mu_1 \sin \frac{2\pi}{\lambda^*} x + \mu_2 \sin \left(\frac{4\pi}{\lambda^*} x + \Delta\right),$$

where μ_0 is the refractive index of the medium in the undisturbed state. The amplitude integral for the intensity at a point, whose join with the origin has its x-direction cosine as 1 is given by

$$\int_{-P/2}^{+P/2} e^{2\pi i \left\{1x - \mu_1 L \sin \frac{2\pi}{\lambda^*} x - \mu_2 L \sin \left(\frac{4\pi}{\lambda^*} x + \Delta\right)/\lambda\right\}} dx \tag{4}$$

where p is the length of the sound beam along the x-axis. Putting

$$u = 2\pi/\lambda,\ b = 2\pi/\lambda^*,\ v_1 = 2\pi\mu_1 L/\lambda \text{ and } v_2 = 2\pi\mu_2 L/\lambda \tag{5}$$

the real and imaginary parts of the integral are

$$\int_{-P/2}^{+P/2} \{\cos ulx \cos [v_1 \sin bx + v_2 \sin (2bx + \Delta) + \sin ulx \sin [v_1 \sin bx + v_2 \sin (2bx + \Delta)]\}\, dx \tag{6}$$

and

$$\int_{-P/2}^{+P/2} \{\sin ulx \cos [v_1 \sin bx + v_2 \sin (2bx + \Delta) - \cos ulx \sin [v_1 \sin bx + v_2 \sin (2bx + \Delta)]\}\, dx \tag{7}$$

Using the well-known Bessel expansions

$$\left.\begin{aligned}
\cos(v\sin bx) &= 2\sum_{0}^{\infty}{}'' J_{2r}\cos 2r\,bx \\
\sin(v\sin bx) &= 2\sum_{0}^{\infty}{}'' J_{2s+1}\sin\overline{2s+1}\,bx \\
\cos(v\cos bx) &= 2\sum_{0}^{\infty}{}''(-1)^r J_{2r}\cos 2r\,bx \\
\sin(v\cos bx) &= 2\sum_{0}^{\infty}{}''(-1)^s J_{2s+1}\cos\overline{2s+1}\,bx
\end{aligned}\right\} \quad (8)$$

the integral of the real part is given by

$$\begin{aligned}
\int_{-P/2}^{+P/2}\{&\cos ulx\,[2\sum_{0}^{\infty}{}'' J_{2r}(v_1)\cos 2r\,bx \times 2\sum_{0}^{\infty}{}'' J_{2s}(v_2)\cos 2s\,\overline{2bx+\Delta} \\
&- 2\sum_{0}^{\infty}{}'' J_{2r+1}(v_1)\sin\overline{2r+1}\,bx \times 2\sum_{0}^{\infty}{}'' J_{2s+1}(v_2)\sin\overline{2s+1}\times\overline{2bx+\Delta}] \\
&+ \sin ulx\,[2\sum_{0}^{\infty}{}'' J_{2r+1}(v_1)\sin\overline{2r+1}\,bx \times 2\sum_{0}^{\infty}{}'' J_{2s}(v_2)\cos 2s\,\overline{2bx+\Delta} \\
&+ 2\sum_{0}^{\infty}{}'' J_{2r}(v_1)\cos 2r\,bx \times 2\sum_{0}^{\infty}{}'' J_{2s+1}(v_2)\sin\overline{2s+1}\times\overline{2bx+\Delta}]\}\,dx \quad (9)
\end{aligned}$$

It can be easily seen that only the first term in the coefficient of cos *ulx* and the second term in the coefficient of sin *ulx* will contribute towards the intensity of even orders and the remaining terms for the intensity of odd orders. The integral for the even term of order $2m$ is given by

$r \pm m$ being even

$$\begin{aligned}
\int_{-P/2}^{+P/2}\{&2\cos ulx\,[\cos(2m\,bx+\Delta.\overline{r+m})\sum_{\delta}^{\infty}{}'' J_{2r}(v_1)\,J_{r+m}(v_2) \\
&+ \cos(2m\,bx-\Delta.\overline{r-m})\sum_{\delta}^{\infty}{}'' J_{2r}(v_1)\,J_{r-m}(v_2)]
\end{aligned}$$

$r \pm m$ being odd

$$\begin{aligned}
&+ 2\sin ulx\,[\sin(2m\,bx+\Delta.\overline{r+m})\sum_{\delta}^{\infty}{}'' J_{2r}(v_1)\,J_{r+m}(v_2) \\
&- \sin(2m\,bx-\Delta.\overline{r-m})\sum_{\delta}^{\infty}{}'' J_{2r}(v_1)\,J_{r-m}(v_2)]\}\,dx, \quad (10)
\end{aligned}$$

where δ is the least possible integer. Double dash over the summation sign indicates that the coefficient of terms $J_0(v_1)\,J_m(v_2)$ is half that of others and of $J_0(v_1)\,J_0(v_2)$ is one-fourth that of others.

Considering odd terms of $2m+1$ order we have

$$r+m+1 \text{ and } r-m \text{ being odd}$$

$$\int_{-P/2}^{+P/2} \{2\cos ulx\,[\cos(\overline{2m+1}\,bx + \Delta\cdot\overline{r+m+1})\sum_{\delta}^{\infty} J_{2r+1}(v_1)\,J_{r+m+1}(v_2)$$

$$+\cos(\overline{2m+1}\cdot bx - \Delta\cdot\overline{r-m})\sum_{\delta}^{\infty} J_{2r+1}(v_1)\,J_{r-m}(v_2)]$$

$$r+m+1 \text{ and } r-m \text{ being even.}$$

$$+2\sin ulx\,[\sin(\overline{2m+1}\,bx + \Delta\,\overline{r+m+1})\sum_{\delta}^{\infty} J_{2r+1}(v_1)\,J_{r+m+1}(v_2)$$

$$-\sin(\overline{2m+1}\,bx - \Delta\cdot\overline{r-m})\sum_{\delta}^{\infty} J_{2r+1}(v_1)\,J_{r-m}(v_2)]\}\,dx \qquad (11)$$

Special cases can be derived from these two integrals by substituting different values for the phase difference Δ.

Case I.—When $\Delta = 0$, we have, for even orders, the integral

$$r \pm m \text{ being even}$$

$$\int_{-P/2}^{+P/2} \{2\cos ulx\cos 2mbx\,[\sum_{\delta}^{\infty} J_{2r}(v_1)\,J_{r+m}(v_2) + \sum_{\delta}^{\infty} J_{2r}(v_1)\,J_{r-m}(v_2)$$

$$r \pm m \text{ being odd}$$

$$+2\sin ulx\sin 2mbx\,[\sum_{\delta}^{\infty} J_{2r}(v_1)\,J_{r+m}(v_2) - \sum_{\delta}^{\infty} J_{2r}(v_1)\,J_{r-m}(v_2)]\}\,dx \qquad (12)$$

Denoting terms in square brackets by $(a+b)/2$ and $(a-b)/2$ respectively, we have

$$\int_{-P/2}^{+P/2} [a\cos(ul-2mb)\,x + b\cos(ul+2mb)\,x]\,dx$$

$$= P\left[a\,\frac{\sin(ul-2mb)\,P/2}{(ul-2mb)\,P/2} + b\,\frac{\sin(ul+2mb)\,P/2}{(ul+2mb)\,P/2}\right]$$

which gives the intensity of $+2m$ order as proportional to a^2 and of $-2m$ order to b^2. The values of a and b given by the relations

$$\left.\begin{aligned} a &= \sum_{0}^{\infty} J_{2r}(v_1)\,J_{r+m}(v_2) + (-1)^{r-m}\sum_{0}^{\infty} J_{2r}(v_1)\,J_{r-m}(v_2) \\ b &= (-1)^{r+m}\sum_{0}^{\infty} J_{2r}(v_1)\,J_{r+m}(v_2) + \sum_{0}^{\infty} J_{2r}(v_1)\,J_{r-m}(v_2) \end{aligned}\right\} \qquad (13)$$

are different, giving different values for the intensity of $\pm 2m$ orders and thus introducing asymmetry in the pattern. Similarly for the odd orders

we have expressions giving asymmetry of the pattern, the intensity of $2m + 1$ order being proportional to $(a')^2$ and of $-(2m + 1)$ order to $(b')^2$ where

$$a' = \sum_{0}^{\infty} J_{2r+1}(v_1)\, J_{r+m+1}(v_2) + (-1)^{r-m+1} \sum_{0}^{\infty} J_{2r+1}(v_1)\, J_{r-m}(v_2)$$

$$b' = (-1)^{r+m} \sum_{0}^{\infty} J_{2r+1}(v_1)\, J_{r+m+1}(v_2) + \sum_{0}^{\infty} J_{2r+1}(v_1)\, J_{r-m}(v_2) \qquad (14)$$

Thus for odd orders as well the pattern is asymmetric. The integral of the imaginary term for this case is zero and hence need not be taken into consideration.

Case II.—When $\Delta = \pi$, it can be easily seen by substituting this value for Δ in (10) and integrating that the integral will be same as (12) except for a sign change for the second term. This change of sign leads to the intensity of $+2m$ order being proportional to b^2 and of $-2m$ order to a^2. Similarly for the odd order spectra the intensity of $2m + 1$ order comes out as proportional to $(b')^2$ and of $-(2m + 1)$ order to $(a')^2$. Thus the intensities of diffraction spectra for this case are the same as those of Case I except that they are reversed, the intensities of positive orders in Case I becoming intensities of negative orders in Case II and so on. This result can be easily obtained from a geometrical construction of the resultant wavefront of the superposed waves.

Case III.—When $\Delta = \frac{\pi}{2}$, the integral of second term in (8) vanishes and hence we have the integral

$r \pm m$ being even

$$\int_{-P/2}^{+P/2} \{2 \cos ulx \cos 2m\, bx\, [(-1)^{r+m/2} \sum_{\delta}^{\infty n} J_{2r}(v_1)\, J_{r+m}(v_2) + (-1)^{r-m/2} \sum_{\delta}^{\infty n} J_{2r}(v_1)\, J_{r-m}(v_2)]\}\, dx \qquad (15)$$

which leads to the same contribution to both the $\pm 2m$ orders, thus maintaining symmetry in the pattern. But for this case the imaginary part is found to give some contribution which is found not to effect the symmetry of the pattern. Thus the case when the ratio of wavelengths is 1 : 2 is treated here for three different phase relations and found that the distribution of intensity of different spectra is different in each case.

It can be shown in a general way that similar results will follow when any even ratio of wavelengths is taken in consideration. Considering two sound waves in phase it can be easily shown that, when the ratio of wavelengths is even, the diffraction pattern will be asymmetric whereas, when

they are in any odd ratio, there will be perfect symmetry in the pattern. Let the wavelengths of the sound waves, which are in phase be λ^* and λ^*/k. Following the usual method, the amplitude integral becomes

$$\int_{-P/2}^{+P/2} \{\cos ulx \,[2 \overset{\infty}{\underset{0}{\Sigma'}} J_{2r}(v_1) \cos 2r\,bx \times 2 \overset{\infty}{\underset{0}{\Sigma'}} J_{2s}(v_2) \cos 2s\,kbx$$
$$- 2 \overset{\infty}{\underset{0}{\Sigma}} J_{2r+1}(v_1) \sin \overline{2r+1}\,bx \times 2 \overset{\infty}{\underset{0}{\Sigma}} J_{2s+1}(v_2) \sin \overline{2s+1}\,kbx$$
$$+ \sin ulx \,[2 \overset{\infty}{\underset{0}{\Sigma}} J_{2r+1}(v_1) \sin \overline{2r+1}\,bx \times 2 \overset{\infty}{\underset{0}{\Sigma'}} J_{2s}(v_2) \cos 2s\,kbx$$
$$- 2 \overset{\infty}{\underset{0}{\Sigma'}} J_{2r}(v_1) \cos 2r\,bx \times 2 \overset{\infty}{\underset{0}{\Sigma}} J_{2s+1}(v_2) \sin \overline{2s+1}\,kbx]\}\,dx \qquad (16)$$

For even orders the first terms in coefficient of cos *ulx* and second term in coefficient of sin *ulx* will contribute. This leads to different expressions for the intensities of $+2m$ and $-2m$ orders. It is the remaining terms which contribute towards the intensity of odd orders and give likewise different values for the intensities of $\pm(2m+1)$ orders. Thus the pattern will on the whole be asymmetric for any even ratio of wavelengths of sound waves superposed in phase. When the value of k is odd all even terms are obtained from the coefficients of cos *ulx* giving same intensity for both $\pm 2m$ orders. Similarly the coefficients of sin *ulx* contribute towards the intensity of odd orders and give the same value for $\pm(2m+1)$ orders. Thus perfect symmetry in the pattern is maintained when the ratio of wavelengths of the sound waves is odd.

The special case when the ratio of wavelengths is 1 : 3 can be obtained be substituting $k = 3$ in (16). The treatment for this case can easily be extended for different phase relations.

3. Calculations and Discussion of the Theoretical Results

With a view to verify the theoretical conclusions, and also to show the nature and magnitude of the asymmetry introduced, intensities of diffraction spectra are calculated for Case I using relations (13) and (14). Table I gives the intensities for different values of the parameters v_1 and v_2. The relative intensities of various orders are represented in Fig. 1 to indicate the nature and extent of asymmetry introduced for different values of v_2 keeping value of v_1 constant. The test for the calculation of the intensities is to be found in the fact that the sum of the intensities of all the spectra is unity as shown in Table I, accounting for the total intensity of the incident light. Though the calculation of the intensities using (13) and (14) involve a summation of infinite series of products of Bessel functions, it is made easy due

TABLE I. $v_1 = 1$

I \ v_2	0	1	2	3
I_0	0·586	0·344	0·030	0·039
I_{+1}	0·194	0·020	0·030	0·078
I_{-1}	0·194	0·299	0·119	0·001
I_{+2}	0·013	0·191	0·257	0·082
I_{-2}	0·013	0·055	0·140	0·055
I_{+3}		0·025	0·100	0·006
I_{-3}		0·053	0·161	0·131
I_{+4}		0·003	0·124	0·199
I_{-4}		0·002	0·036	0·088
I_{+5}			0·012	0·007
I_{-5}			0·040	0·117
I_{+6}			0·021	0·094
I_{-6}			0·003	0·027
I_{+7}			0·002	0·008
I_{-7}			0·004	0·034
I_{+8}			0·002	0·020
I_{-8}				0·004
ΣI	1·000	0·992	0·991	0·990

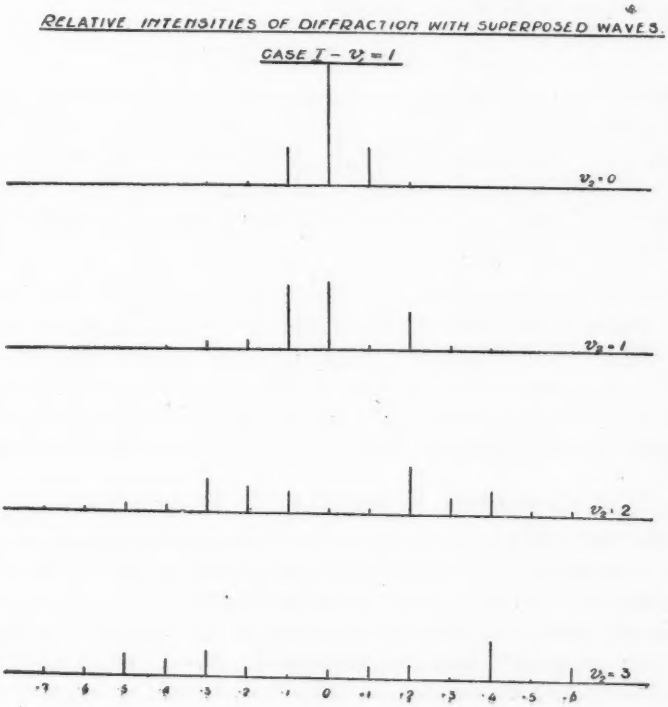


FIG. 1

to the fact that they are very rapidly convergent series so that, in most of the cases, only the first two terms of the series need be taken into account.

A remarkable feature that comes out from the calculations is that for lower values of v_1 and v_2 in general the odd order diffraction spectra are stronger on the negative side while the even orders are stronger on the positive side of the central image. Thus the -1 order is stronger than the $+1$ order, the $+2$ order is stronger than -2 order, and so on. The nature of the asymmetry introduced in this case is thus entirely different from the oblique incidence asymmetry in which most of the light will be thrown on one side of the central image making the orders on the appropriate side stronger than the corresponding orders ont the other side.

In conclusion, it may be pointed out that the same type of results can also be obtained from the rigorous theory of Raman and Nath. The theory can also be generalised to the case of diffraction of light by special types of waves like the saw-tooth wave, the diffraction effect of which can be obtained by considering it as a superposition of a number of sine waves with frequencies in integral ratios and in phase.

4. Experimental Details

With a view to verify the theoretical conclusions qualitatively, the experimental investigation is taken up by the author, the study being limited to Case I involving two sound waves with frequencies in ratio 1 : 2 and in phase. While all the previous investigators employed stationary waves it is essential for this investigation to use progressive sound waves to obtain the results predicted by the theory.

For setting up progressive sound waves in water, a long tank of $1\frac{1}{2}$ metres height is made with tin sheet and is provided with two glass windows at the top to allow the passage of light. The bottom of the tank is stuffed with felt and glass wool preventing the reflection of the sound wave and thus giving an ideal progressive sound wave. The arrangement for obtaining and recording diffraction spectra is the usual one similar to that of Debye and Sears.

Radio waves which are in phase and one of which is an octave of the other are generated by employing two different types of harmonic generator circuits. Both types of circuits are employed for obtaining the diffraction spectra but the one that is most convenient and powerful is shown in Fig. 2. The circuit employs an oscillator constructed with 813 valve whose output is fed into a regular harmonic generator circuit. The harmonic generator employs a Taylor T55 valve with a tank circuit, tuned to the second harmonic

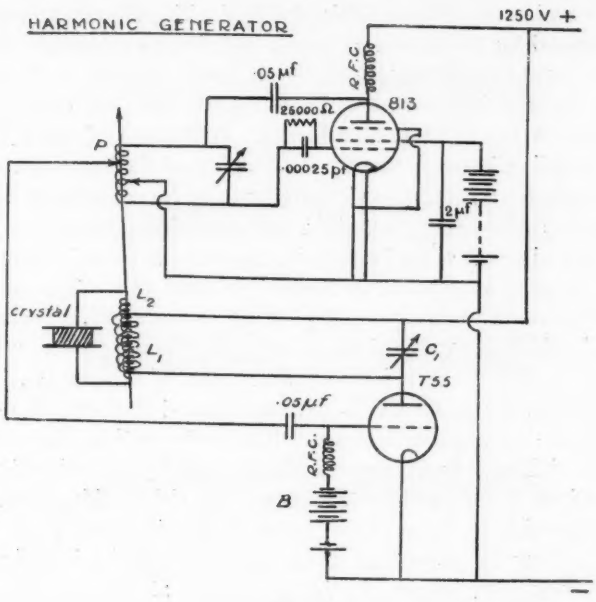


FIG. 2

of the oscillator, as the load impedance and with a variable grid bias B obtained from a 500 volt power supply unit. The bias B and the tapping point P are adjusted to generate the second harmonic of the oscillator powerfully. Coupled to inductance coil L_1 of the harmonic generator there is another coil L_2 which is connected across the crystal. The coil L_2 being coupled to both to the oscillator and the harmonic generator draws energy from both. With this type of circuit it has been possible to obtain diffraction spectra upto a large number of orders. A quartz *x*-cut plate of thickness 2·5 mm. and a fundamental frequency of about 1·2 Mcs. is employed for the investigation. The quartz plate which is silvered uniformly and nickel plated on both its surfaces is coupled to the circuit as shown in Fig. 2.

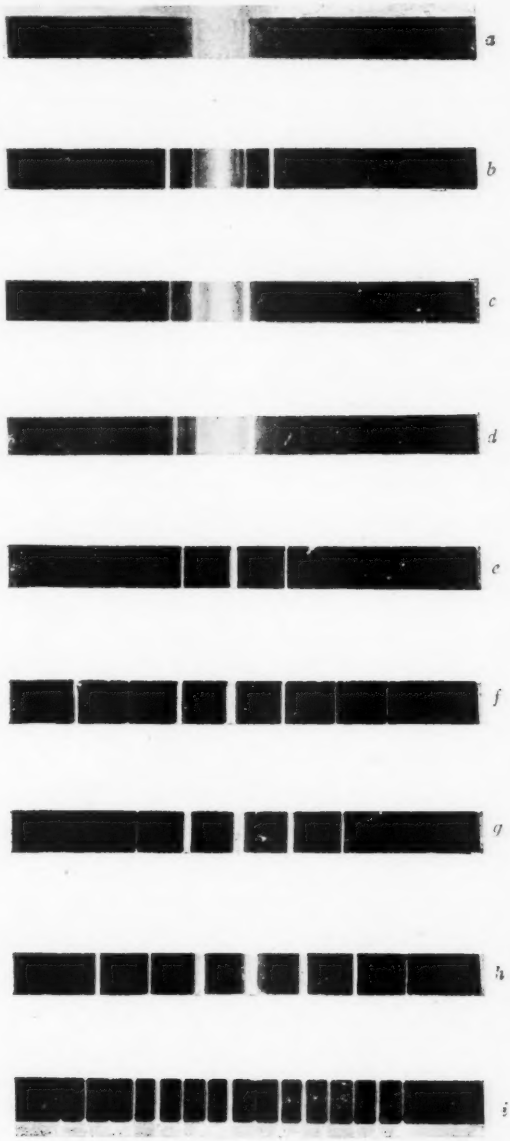
5. Discussion of the Photographs of Diffraction Spectra

Diffraction spectra obtained for different frequencies under varying excitation conditions are shown in Plate I. Plate I (*a*) and (*b*) show patterns obtained with sound waves of frequencies 3 Mcs. and 6 Mcs. respectively. The patterns obtained by combining these two waves in phase are shown in Plate I (*c*) and (*d*). Plate I (*c*) brings out the asymmetry obtained by superposition very clearly, the 2 order being obtained very strongly compared with

the -2 order and so on. Plate I (*d*) is obtained with different power of excitation of the crystal for the second harmonic and shows conspicuous asymmetry. Exciting the crystal at 6 Mcs. and its second harmonic at 12 Mcs. Plate I (*e*) to (*h*) are obtained. In all these cases it has not been possible to isolate the pattern for 12 Mcs. sound wave. In Plates I (*e*) and (*f*) obtained with loose coupling between the crystal circuit and the harmonic generator, (*e*) corresponds to 6 Mcs. sound wave and (*f*) corresponds to patterns obtained with superposed sound waves showing marked asymmetry. Patterns obtained at the same frequencies but with increased power of excitation of the crystal, are shown in Plate I (*g*) and (*h*). Though the total intensity is increased, the asymmetry is still maintained. The alternating intensities of odd and even orders, pointed out in the previous theoretical investigation, is clearly seen in both the Plate I (*f*) and (*h*). In Plate I (*h*), for example, the -1 order is stronger than $+1$ order, the $+2$ order is stronger than -2 order and so on. It must be noticed that this type of asymmetry is different from that of the asymmetry introduced by tilting where the diffracted light will be thrown on one side making each order on the appropriate side stronger than the corresponding order on the other side. With a view to show that no asymmetry will be introduced when two sound waves with frequencies in the ratio 1 : 3 are superposed, Plate I (*i*) is obtained with 6 Mcs. and 18 Mcs. sound waves. The harmonic generator is biased to give the third harmonic very strongly and the tank circuit is tuned to the third harmonic of the oscillator circuit. Pattern thus obtained showed a number of combination lines on either side of the central image without any loss in the symmetry of the pattern. Thus in a general qualitative manner the results predicted by the theoretical investigation are experimentally confirmed.

6. Summary

Employing Raman and Nath's simplified theory, the author has investigated the diffraction effects that are to be expected when the ultrasonic wave is obtained by a combination of two sound waves with frequencies in 1 : 2 ratio superposed in different phases. Intensities of individual diffraction orders have been calculated from expressions derived for the case of two sound waves of frequencies in 1 : 2 ratio superposed in phase. The type of asymmetry introduced in this case is found to be different from the oblique incidence asymmetry. The treatment is also generalised to the case of superposition of two sound waves with frequencies in any odd or even integral ratios. The theoretical results have been experimentally confirmed in a qualitative manner by employing special type of harmonic generator circuits.


a
b
c
d
e
f
g
h
i

In conclusion, the author wishes to express his grateful thanks to Prof. S. Bhagavantam for the keen interest he has shown during the progress of the work.

References

1. P. Debye and F. W. Sears .. *Proc. Nat. Aead. Sci.*, 1932, **18**, 410.
2. R. Lucas and P. Biquard .. *C. R. Acad. Sci.*, 1932, **194**, 2132.
3. C. V. Raman and N. S. N. Nath .. *Proc. Ind. Acad. Sci.*, 1935, **2** A, 406.
4. L. Bergmann .. *Zs. f. Hochfrequenztechnique*, 1934, **43**, 83.
5. ——— and E. Fues .. *Zs. f. Physik.*, 1938, **109**, 1.
6. M. A. Govinda Rao .. *Proc. Ind. Acad. Sci.*, 1938, **8** A, 6.
7. E. Hiedemann and K. H. Hosch .. *Zs. f. Physik.*, 1935, **98**, 141.
8. N. S. N. Nath .. *Cam. Phil. Soc. Proc.*. 1938, **34**, 213.
9. K. Nagabhushana Rao .. *Proc. Ind. Acad. Sci.*, 1938, **8** A, 124.

SPECTRAL SENSITIVITY OF *JOSHI-EFFECT* IN CHLORINE

By P. G. Deo, Ph.D., D.Sc.

(*Department of Physics, University of Saugor, Saugor*)

Received October 13, 1948

(Communicated by Dr. S. S. Joshi, F.A.Sc.)

The marked dependence of this phenomenon Δi, on the nature of irradiation, was suggested by earlier results (Joshi, 1943, 1945; Deo, 1944). Attempts, since in progress to investigate this relationship in some detail, were, however, confronted with difficulties in securing monochromatic bands in different parts of the spectrum, of adequate intensity under comparable conditions. Line sources such as mercury, carbon, iron and other arcs employed by the author previously (Deo, 1943, 1944) were found unsuitable because of their unsteady intensity conditions. The results now reported were obtained with a continuous source; the effective frequency of irradiation (restricted to the visible) was altered by introducing selected coloured glass strips and Kodak Wratten filters between the light source and the ozoniser. In order to obtain the adequate intensity, the filtered band in some cases comprised a spectral region as wide as 1000 A.

Experimental Part

A transformer discharge of 50 cycles (primary) frequency was produced in annular space of a Siemens' type glass ozoniser filled with purified chlorine at a pressure of 11 cm. Hg. The ozoniser was irradiated directly or through one of the filters, by a 500 watt, 180 volt incandescent (glass) bulb; the direction of irradiation was parallel to ozoniser axis. At a given exciting potential kV, observations of the current (*vide infra*) were made as follows: (i) when the ozoniser was in dark; (ii) when exposed directly to (unfiltered) white from the above light sources, and (iii) to one of the filtered bands, and lastly (iv) to the light from a sodium vapour lamp. The ozoniser current i was measured with a Cambridge vacuo-junction connected to a sensitive mirror galvanometer. The values i are shown below the corresponding galvanometer deflections ai^2 and placed within brackets, at a given kV, in dark and in various frequency bands in Table 1.

The spectral limits of the unfiltered white, and of the transmission through the various filters used were observed with a Fuess instrument.

TABLE I

Production of Joshi-Effect *in Chlorine in Different Spectral Regions*

kV	In dark	White (7800–3700 A)	Ordinary filter Nos. 1 (7070–6070A)	2 (5775–5070A)	3 (4750–4000A)	Wratten filter Nos. 70 (7100–6100A)	72 (6400–5900A)	73 (6000–5600A)	74 (5700–5150A)	75 (5200–4650A)	76 (4850–4300A)	Sodium lamp (5896–5890A)
2·9	(13)	(1)	(10)	(8)	(1)	(12)	(10)	(8)	(5)	(4)	(3)	(6)
	3·6	1·0	3·2	2·8	1·0	3·5	3·2	2·8	2·2	2·0	1·7	2·4
	Δi	2·6	0·4	0·8	2·6	0·1	0·4	0·8	1·4	1·6	1·9	1·2
	$\%\Delta i$	72·2	11·1	22·2	72·2	2·8	11·1	22·2	38·8	44·4	51·1	33·3
3·2	(31)	(4)	(22)	(17)	(4)	(24)	(21)	(18)	(12)	(8)	(.)	(15)
	5·6	2·0	4·7	4·1	2·0	4·9	4·5	4·2	3·5	2·8	2·7	3·8
	Δi	3·6	0·9	1·5	3·6	0·7	1·1	1·4	2·1	2·8	2·9	1·8
	$\%\Delta i$	64·3	16·1	26·8	64·3	12·5	19·6	25·0	37·5	50·0	51·8	32·2
3·5	(49)	(9)	(45)	(29)	(11)	(44)	(40)	(36)	(22)	(18)	(16)	(30)
	7·0	3·0	6·7	5·4	3·3	6·6	6·3	6·0	4·7	4·2	4·0	5·5
	Δi	4·0	0·3	1·6	3·7	0·4	0·7	1·0	2·3	2·8	3·0	1·5
	$\%\Delta i$	57·1	4·3	22·8	52·8	5·7	10·0	14·2	32·8	40·0	42·8	21·4
3·7	(86)	(19)	(74)	(54)	(24)	(74)	(69)	(63)	(46)	(34)	(34)	(50)
	9·3	4·4	8·6	7·4	4·9	8·6	8·3	7·9	6·8	5·8	5·8	7·1
	Δi	4·9	0·7	1·9	4·4	0·7	1·0	1·4	2·5	3·5	3·5	2·2
	$\%\Delta i$	52·7	7·5	20·4	47·3	7·5	10·8	15·0	26·8	38·5	38·5	23·6
4·0	(125)	(44)	(112)	(84)	(46)	(109)	(101)	(93)	(75)	(63)	(56)	(81)
	11·2	6·6	10·6	9·2	6·8	10·4	10·1	9·6	8·7	7·9	7·5	9·0
	Δi	4·6	0·6	2·0	4·4	0·8	1·1	1·6	2·5	3·3	3·7	2·2
	$\%\Delta i$	41·1	5·3	17·8	39·2	7·2	9·8	14·4	22·3	29·4	33·0	19·6
4·5	(169)	(64)	(155)	(122)	(73)	(154)	(143)	(137)	(110)	(95)	(93)	(116)
	13·0	8·0	12·5	11·1	8·5	12·4	12·0	11·7	10·5	9·8	9·6	10·8
	Δi	5·0	0·5	1·9	4·5	0·6	1·0	1·3	2·5	3·2	3·4	2·2
	$\%\Delta i$	38·4	3·8	14·6	34·6	4·6	7·7	10·0	19·2	24·6	26·1	16·9
5·1	(206)	(89)	(192)	(156)	(100)	(190)	(180)	(172)	(144)	(128)	(124)	(156)
	14·4	9·4	13·9	12·5	10·0	13·8	13·4	13·1	12·0	11·3	11·1	12·5
	Δi	5·0	0·5	1·9	4·4	0·6	1·0	1·3	2·4	3·1	3·3	1·9
	$\%\Delta i$	34·7	3·5	13·2	30·6	4·1	7·0	9·0	16·6	21·5	22·9	13·2
Relative Intensity I												
With Photo-cell		253	109	0·1	107	179	90	117	81	56	71	
,, Thermopile		50	21	0·1	13	41	25	25	24	25	28	
Above with CS_2+I_2 filter		*104	66	1–2	15	91	90	87	90	83	80	

* The corresponding value for white, without filter, is 143.

Their relative intensities I were measured with R.C.A. 918 Cæsium coated photo-cell and also Kipp's 37 surface thermopile. These data are shown at the bottom of Table I in appropriate columns (*re.* other intensity data with iodine filters, *vide infra*).

The current voltage characteristic, in dark and corresponding to each of the above spectral regions are shown in Fig. 1.

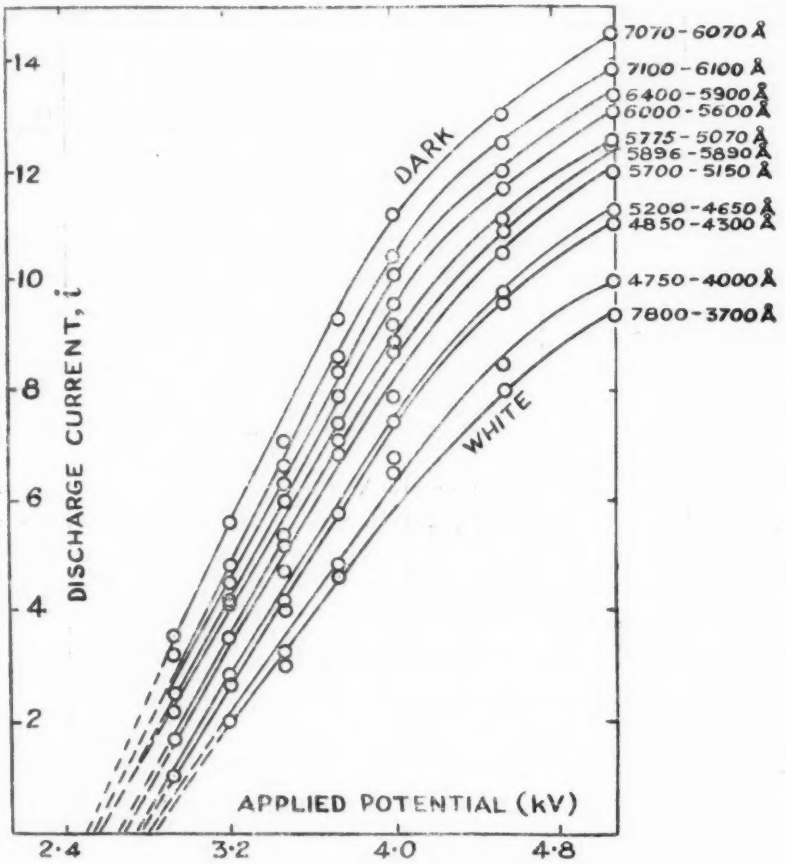


FIG. 1. Potential–Current Characteristics in Various Spectral Regions

DISCUSSION

Results in Table I show the production of *Joshi-Effect* in the range 34–72% current decrease—instantaneous and fully reversible—under the unfiltered white. Whilst the net effect increases with the applied kV, the relative *effect* $\%\triangle i$ decreases appreciably.

Despite the very pronounced differences in the intensity of the filtered bands, it is remarkable that in agreement with the earlier results (Joshi and

Deo, 1943; Deo, 1943), the disposition of the characteristic V-*i* curves is frequency wise (Fig. 1). At a given V, the magnitude of the phenomenon increase from red to violet. The work of Halban and Siendentopf (1922) and others shows that the absorption coefficient of chlorine rises rapidly with frequency in the short wavelength region, especially above its threshold limit, 4785 A. In fact, chlorine derives its colour by light absorption in the band 2300–5000 A. That this might explain the marked *Joshi-Effect* under the unfiltered white (7800–3700 A) where it is maximum and in the band 4750–4000 A, meets with the difficulty in the production of about 13–33% *Joshi-Effect* in the sodium light (5890–5896 A) which is fairly outside the absorption band, and especially Joshi's observation (1945) of an appreciable $\%\Delta i$ even at 7700 A and longer where absorption by chlorine is negligibly small. These results are in accord with Joshi's view (1943) that Δi is not (entirely) the consequence of selective light absorption, but rather a quantum or frequency effect.

It is instructive to consider the current potential characteristic curves (Fig. 1) when the ozoniser was in dark, and irradiated in the various wavelengths. Joshi (1929, 1931, 1939, 1944) has shown, on the basis of considerable amount of experimental and theoretical evidence, (1) that the ozoniser current i depends upon $V–V_m$ and (2) that the V_m increases if under a given change, the electron affinity of the product exceeds that of the antecedent material. From his observation of an increase of V_m under light Joshi predicted and actually observed (1939) the effect Δi. It is to be anticipated therefore, that the 'threshold potential' V_m under light should be greater, the larger its mean frequency. Results of the extrapolation of the above curves on the potential axis, indicate that this is so.

It is seen from data in Table I that the *Joshi-Effect* under unfiltered white (Δi_{white}) is sensibly less than $\Sigma\Delta i$, *i.e.*, the sum of the corresponding values of the net effect observed in both the series of filtered bands. Thus *e.g.*, at 4.5 kV, Δi_{white} is 5.0, as against 6.9 for $\Sigma\Delta i$ for the three components using ordinary glass filters. The corresponding quantity ($\Sigma\Delta i$) for the six bands using the various Wratten filters, is 12.0. An apparently similar result is noticed for I, the intensity: with a photo-electric cell, I_{white} was 253; ΣI, however, for say, the Wratten filters was 594. A like disparity obtains in data with the thermopile. Since 'saturation' is not likely with a thermopile and a vacuum type photo-electric cell, a common leak (*i.e.* infra-red) was looked for: A glass cell with a saturated solution of iodine in carbon disulphide was interposed between the thermopile and each of the light source (Table I); practically only the infra red is transmitted. Its intensities are shown at the bottom of Table I. The iodine filter

transmits about 80%; of which, for the Wratten filters, 60–65% is a common leak, making $\Sigma I > I_{white}$.

It is found that the *Joshi-Effect* is negligibly small in the infra-red (Joshi and Deo, 1943). Besides, a spectroscopic examination of the transmissions by each of the above filters showed that they had no sensible common leaks. The excess of $\Sigma \Delta i$ over Δi white may be attributed therefore, to saturation (Deo, 1944).

Joshi (1929) has shown that approximately the discharge current i is given by,

$$i = \frac{\alpha U_-}{Z},$$

where α is Townsend's coefficient of ionisation for an electron and depends upon U_-, the velocity of the electron; and Z is the coefficient of ionic recombination.

A decrease of i under light might originate therefore, from either/and a decrease of U_- and increase of Z. Undertaken at Prof. Joshi's suggestion, work is in progress to investigate if in the spectrum of the excited chlorine under conditions productive of a large Δi, an increase in Z occurs. The other quantity U_- is expected to decrease due to an increase in electron affinity of the medium and causing an increase of the corresponding V_m. Franck (Townsend, 1915) showed that (under weak fields) U_- in pure argon and nitrogen diminished by about 100 times due to admixture of about 2% of oxygen. Similar result was observed by Mayer (1926) in oxygen due to admixture of about 1% of chlorine. Now according to Franck (Loeb, 1939, except for its low energy of dissociation (1.5 e.v.) a chlorine molecule is inert chemically and should have no electron affinity. The energy release on the attachment of an electron to a chlorine atom is 4.1 e.v. Franck suggested that the capture of an electron by a chlorine molecule is immediately followed by its dissociation into atoms. This is supported by the mass spectrographic studies of Dechend and Hammer (1911) which indicate the existene of negative atomic chlorine ions and not molecular ions in canal rays. The photo-dissociation of chlorine molecule into atoms occurs under frequencies $>$ 4785 A, its threshold limit. This would increase the electron affinity of the system and cause a decrease in the discharge current and favour Δi, the *Joshi-Effect*.

The results in Fig. 2 relate the mean frequency in the various bands with the corresponding *Joshi-Effect* $\%\Delta i$. It is significant that a sensibly linear relation is seen in practically all the series. When, however, the operative conditions were varied over a wide range, the above relation did

not hold. A linear relation between Δi and the light frequency follows simply from Joshi's theory (1945, 1946, 1947) that photo-electric emission

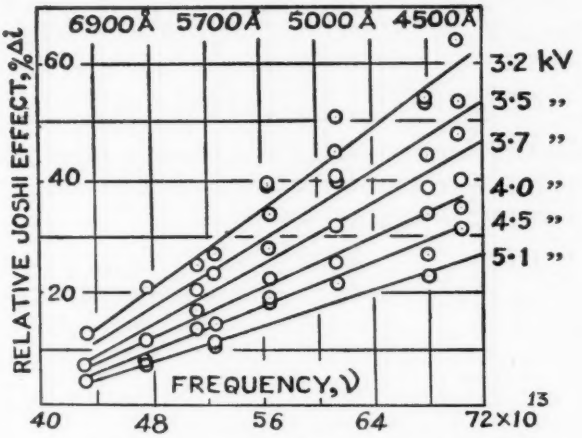


FIG. 2. Frequency Influence on *Joshi-Effect* in Chlorine.

from a boundary layer (formed, in part, from an adsorption of the ions and excited molecules), is primary to the *effect* Δi. Deviation from the linear relation mentioned above, might originate from such limiting factors as 'saturation' and superimposition of secondary changes on the primary photo-electric effect. A linearity similar to that in Fig. 2, has been observed recently by B. N. Prasad (1946) working at Benares, in excited mercury vapour. It may be observed that at a given kV the extrapolation of the $\%\Delta i - \nu$ curve to the frequency-axis gives the magnitude of the corresponding work function of the postulated photo-active boundary layer formed under discharge; *e.g.* its value corresponds to about 8130 A at 3·2 kV.

Grateful thanks are due to Professor S. S. Joshi, D.Sc. (London), F.R.I.C. (London), F.A.Sc., F.N.I., Principal, College of Science, Benares, Hindu University, for facilities to work, kind interest and valuable suggestions.

SUMMARY

Joshi-Effect—an instantaneous and reversible diminution Δi of discharge current i—is studied in 11 cm. chlorine excited by the silent discharge from 2 to 6 kV of 50 cycles frequency under light from a sodium vapour lamp, that from an incandescent (glass) bulb, directly; and with Wratten and other filters. Relative *Joshi-Effect* $\%\Delta i = 100\ \Delta i/i_D$ at maximum is 33%

sodium light and 72% under unfiltered white. Observed with a thermopile (also with a photo-electric cell) the light intensity lay in the order, unfiltered white (50), violet (13), green (0.1) and red (21). The effect, however, varies, frequencywise. Large Δi under sodium light and red, as observed, support Joshi's view that Δi is a quantum or frequency effect and not (entirely) a consequence of selective light-adsorption. Under a limited range of conditions, the curves $\%\Delta i$—mean light frequency (ν) are almost straight lines at a series of kV, which follows simply from Joshi's theory that a photo-electric effect from an adsorption-like boundary layer formed under the discharge is a primary change precedent to Δi.

References

Joshi .. *Trans. Farad. Soc.*, 1929, **25**, 108, 118, 143.

———— .. *Proc. Ind. Sci. Cong., Chem. Sec.*, 1931, *Abst.* 63.

———— .. *Curr. Sci.*, 1939, **8**, 548.

——— and Narsimhan .. *Ibid.*, 1940, **9**, 536.

Joshi .. *Proc. Ind. Sci. Cong.* (Presidential Address, Chem. Sec.), 1943.

———— .. *B.H.U. Journ.*, 1943, **8**, 103.

——— and Deo .. *Nature*, 1943, **151**, 561.

———— .. *Curr. Sci.*, 1943, **11**, 306.

Deo .. *Ind. Journ. Phys.*, 1944, **18**, 84.

———— .. *Proc. Ind. Acad. Sci.*, 1944, **19**, 117.

Joshi .. *Nature*, 1944, **154**, 147.

———— .. *Curr. Sci.*, 1945, **14**, 317.

Prasad, B. N. .. *Unpublished results*, 1946.

Joshi .. *Proc. Ind. Sci. Cong., Phys. Sec.*, 1946, *Abst.* 26.

———— .. *Ibid.*, 1947.

———— .. *Curr. Sci.*, 1947, **16**, 19.

Dechend and Hammer .. *Jahrb. Rad. Und. Elektron*, 1911, **8**, 77.

Townsend .. *Electricity in Gases*, Oxford, 327, 380.

Halban and Siedentopf .. *Z. Phys. Chem.*, 1922, **103**, 71.

Mayer .. *Phys. Z.*, 1926, **27**, 513.

Loeb .. *Fundamental Processes of Electrical Discharge in Gases*, John Wiley & Sons, 1939, pp. 285, 408.

GEOLOGY AND PETROLOGY OF PACHIPENTA ZAMINDARI, VIZAGAPATAM DISTRICT, MADRAS PRESIDENCY

By G. Gopalakrishna Sastri, M.Sc.

Received August 2, 1948
(Communicated by Prof. C. Mahadevan, F.A.SC.)

Introduction

Pachipenta is a small Zamindari in the hill tracts of the Vizagapatam District, lying between longitudes 83° 3′ and 83° 10′ E. and latitudes 18° 26′ and 18° 32′ N. Surrounded by Salur Zamindari in the North, Vizianagaram Zamindari in East and South and Jeypore State in the West, it lies near the provincial boundary between Madras and Orissa. The well-known "Jeypore Ghat Road" leading from Salur up the precipitous slopes of Eastern Ghats to Jeypore runs at a distance of 3 miles from Pachipenta Village, the capital of the Zamindari. Foot paths form the only means of communication in the area and the villages are inhabited mostly by the hill tribes.

Previous Literature

The area under report lies in the "Eastern Ghats Province" in the "Charnockitic region" of Sir L. L. Fermor (1935) and has not been studied by any geologist so far. However the works of Benza (1837), Carmichael (1869), W. King (1886), F. H. Smith (1889–1900), Walker (1902), Middlemiss (1904), Mahadevan (1929) and Crookshank (1938) on the geology of the neighbouring tracts in Vizagapatam District and Jeypore State deal with more or less similar formations.

Physiography

The area presents a rugged topography with low-lying plains encircled by chains of mountains. The general elevation of the plains is about 700′ while the maximum elevation of the mountains is about 2,000′. River Vegavati is the main drainage channel of the area. Taking its birth far in the interior of the Jeypore State, it flows through long narrow valleys and comes down to the plains at a locality called "Sankellagummi", where it takes a leap of 15′ to 20′ and falls in a chasm amidst forest surroundings of exquisite beauty. It has numerous tributaries which are dry for a greater part of the year. The river is, however, perennial with a shrunken summer

flow. This is mainly due to the fact that the water-bearing porous sandy layers dip from the hills towards the river. There are two small springs and many other seepages. Rock exposures are few and far between due to the dense forests and the thick soil covering the mountains.

Geological Formations

Various members of the Khondalite series and charnockites intrusive into them are the formations met with in the area. The succession of rocks belonging to the khondalite series and consisting of arenaceous, argillaceous and calcareous members was carefully studied and the following sequence has been arrived at:

Charnockites

Crystalline limestones Diopside quartzites Garnet sillimanite gneisses Garnetiferous gneisses Biotite gneisses and mica schists	Khondalite series.

Khondalite Series

(*a*) *Biotite gneiss.*—The predominant rock type and one which apparently is the oldest member of the series is a highly quartzitic gneiss with subordinate felspar, biotite and garnet, conveniently termed biotite-gneiss. In the northern part of the area the rocks have a strike of N.W.-S.E. and dip at 30° to 60° towards S.W. In the southern part, however, the strike is E.N.E. and the dip, 50°–60° towards S.S.E. Local variations in strike are very common. The rocks are well bedded and medium to fine-grained. Graphite is an occasional accessory.

(*b*) *Mica schist.*—Biotite schists occur interbanded with these gneisses in some localities. The rocks have the same trend as the gneisses and are seen to consist mostly of biotite with a little garnet.

(*c*) *Garnetiferous gneiss.*—Succeeding the schists and gneisses occur the garnetiferous gneisses. They have a strike of E.N.E. and a dip of 50° to 60° towards S.S.E. They are coarse-grained and consist of folia of quartz and felspar alternating with those of garnet and biotite. The felspar occurs in good sized laths arranged linearly in the direction N.W.-S.E.

(*d*) *Sillimanite-garnet gneisses.*—Exposed on the hillock, Masimetta, is another rock type which can be called a cordierite-sillimanite-garnet gneiss. The rocks have a strike of W.N.W. and dip at angles of 30° to 35° towards S.S.W. Folia of quartz, felspar and cordierite alternate with those of garnet, sillimanite and hypersthene. The stratigraphic sequence of these rocks is not

free from obscurity as the exposure is isolated. Nevertheless, since they too are traversed by dykes of charnockites and since they apparently represent metamorphosed sediments rich in alumina, they are considered to belong to the khondalite series and are given a position above the garnetiferous gneisses.

(*e*) *Diopside quartzites.*—The calcareous members of the khondalites are exposed on Lingalametta. The prevalent rocks are the diopside quartzites which are mostly massive but exhibiting a marked fissility in the direction N. 10° W. in the lower portions of the hillock. River cuttings expose small folds and plications into which the rocks were thrown. The rocks are fine-grained and consist of quartz and diopside, the latter mineral imparting a green colour to the rock. The structural features of this rock evidently point to its original sedimentary nature. Because of its association with crystalline limestone, it is placed above the argillaceous members of the series.

(*f*) *Crystalline limestone.*—Bands of crystalline limestone occur associated with diopside quartzites on the same hillock. There are two bands each 10′ wide trending in the direction N. 40° W. and extending for a distance of about 2 furlongs. The rocks are made up mostly of crystals of calcite enclosing small grains of diopside. Being evidently a metamorphosed limestone, it is considered to be the youngest member of the series.

Geological Age

These formations are then evidently highly metamorphosed sediments which have been intruded by charnockites. The abundance of hypometamorphic minerals and the occurrence of crystalline limestones in association indicate affinties with the middle division of the Dharwars.

Charnockites

In various localities, the khondalites are traversed by narrow dykes of charnockites. Only the basic type consisting of plagioclase, rhombic and monoclinic pyroxenes, magnetite and a little quartz is represented here. The rocks are allied to the augite norites of the type area. They are dark coloured, medium to fine-grained and compact. They usually follow the strike of the gneisses which they invade but were seen occasionally to cut across. No major contact phenomena are to be noticed.

Lastly, mention must be made of the pegmatites and quartz veins traversing the area. The latter are of no interest. On △ 1379 pegmatites are seen to cut across khondalites and charnockites. Pegmatites traversing mica schists often contain books of muscovite mica in pockets up to 6″ in

cross-section. Some of them, as those near Yerravadlavalasa and Kagulageda seem to be economically workable. Other pegmatites contain such minerals as recrystallised garnets and tourmaline. Diopside, in good sized crystals, occurs in a pegmatite exposed in the vicinity of the crystalline limestone bands on Lingalametta.

MINERALOGY

Mineralogy of the Members of the Khondalite Series

Alkali felspar.—The felspar of the khondalites of Vizagapatam District has been described by King as murchisonite, "a peculiar brilliantly glistening, bronze-red, flesh coloured or even white mineral most easily cleaved in two directions". Dr. P. M. Benza calls a similar felspar from the Bezwada gneiss cleavlandite, a variety of albite. Chemical analysis of the rocks show a preponderance of potash over soda and the felspar noted under the microscope is mostly orthoclase. Hence it is likely that the felspar from the khondalites of the area is orthoclase or its variety murchisonite and not albite. The felspar in these rocks is highly altered.

Plagioclase is very subordinate to potash felspar and exhibits a typical lamellar twinning. It is an acid variety corresponding to albite-oligoclase or oligoclase. The anorthite content could not be determined since this too shows a high degree of alteration.

Quartz is present in all the members except the crystalline limestones It is usually colourless and between crossed nicols occasionally exhibits undulose extinction.

Garnet is present in all but the calcareous members. It is developed in rounded grains of variable size. Under the microscope, it has a high refractive index and pale pink colour and is isotropic. It is commonly traversed by numerous cracks. Often it is diablastic with inclusions of quartz, hypersthene, biotite, magnetite and sillimanite.

The garnets are arranged in parallel bands bringing out the gneissose nature of the rock. They are also elongated parallel to the gneissic planes. Local alteration to chlorite and biotite is noticed.

Sillimanite is found only in two rock types where it is abundantly developed. The high refractive index and second order polarisation colours are of help in identifying the mineral under the microscope. It is colourless and occurs in slender prisms and rounded grains. It is often found in clusters associated with hypersthene and magnetite. It is also seen as inclusions in garnet.

Cordierite is an important constituent of some members of the khondalite series. It occurs either disseminated in the rock or in small pockets. It is optically positive with an optic axial angle of 74°. It contains many pleochroic haloes and exhibits twinning. In chemical composition it is similar to the normal cordierite in spite of its anomalous optic sign (1948).

Hypersthene is present in the cordierite-bearing rock types. It is readily made out under the microscope by its high refringence and birefringence and strong pleochroism from pinkish brown to bluish green. It occurs as small individuals with irregular outlines and frequently with one set of cleavages, with reference to which inclined extinction of about 30° is noted. This fact has already been noticed by Walker (1907).

Biotite is an important accessory in many gneisses and is the chief constituent of the mica schists. It has an intense colour and strong pleochroism from pale yellow to dark reddish brown. The flakes are usually torn and bent and contain pleochroic haloes. Secondary biotite derived from garnet is also seen.

Graphite makes up about 10% of the gneisses from Sudikonda near Alluru. It occurs as needles and flakes arranged along the foliation planes It shows a rugged outline under the microscope and is opaque.

Calcite is the chief mineral of the crystalline limestones. It exhibits typical rhombohedral cleavage and twinkling. Two sets of cleavages are present at an angle of 55° and a third set bisects the angle between them.

Diopside occurs as small irregular grains in the diopside quartzites and crystalline limestones. It is colourless or very pale green. The grains are often traversed by a set of coarse cleavages with an extinction angle of about 45°.

Magnetite and apatite are common as accessories in the various rock types.

Mineralogy of the Charnockites

Felspar forms about 50% of the charnockites and is the chief salic mineral All of it is plagioclase approaching andesine or labradorite in composition. It is optically + ve with a 2 V of 82° corresponding to 64% anorthite content. The characteristic lamellar twinning is seen but the mineral does not show signs of extensive alteration.

Hypersthene is the mineral characteristic of the charnockite series and is abundantly developed in the norites from the area. It has a high refractive

index and polarises in pinks and blues. It is intensely pleochroic, the scheme being,

X : Pinkish brown, Y : Pinkish yellow, Z : Deep green.

The mineral is optically negative with a 2V of 60°. One set of cleavages is prominently developed, with reference to which certain grains show oblique extinction of as much as 30° to 35°. This phenomenon has previously been noticed in other occurrences by Lacroix (1891), Sen Gupta (1916), Walker (1902), Washington (1916), Hess and Phillips (1938) and Johannsen (1939). The oblique extinction is perhaps due to the fact that the sections under consideration are inclined to the three crystallographic axes, as pointed out by Johannsen.

Opaque inclusions of magnetite are commonly seen in the grains of hypersthene.

Augite though subordinate to hypersthene, is an important constituent of the rocks. It occurs in irregular grains traversed usually by one set of cleavages and rarely by two sets intersecting nearly at right angles. The pleochroic scheme of the mineral is

X: Yellowish green, Y: Green, Z: Pale bluish green.

It is optically positive with a 2V of $50° \pm 2°$. The angular distance between the vertical crystallographic axis and the axis of minimum elasticity is about 46°. Schiller inclusions of magnetite are commonly seen.

Hornblende is developed only to a very minor extent and is in almost all cases secondarily derived from the pyroxenes.

Quartz is found in very small quantities and is dark grey in the hand specimens. Under the microscope, it is seen to occur in allotriomorphic and clear grains with occasional wavy extinction.

As accessories, magnetite and apatite are common.

Petrography and Chemical Analyses of Rock Types

Type A

Garnetiferous gneiss.—It is abundantly found in the area. It differs from a typical khondalite in the absence of sillimanite and graphite. The microscope reveals a well-developed gneissic structure with alternating folia of quartz and felspar and garnet, biotite and magnetite.

A fresh specimen with a specific gravity of 2·79 was chemically analysed. The results are given in Table I.

TABLE I

Analyses of Garnetiferous Gneiss and Comparable Rocks

	AA	AB	AC	AD	AE	AF
SiO_2 ..	67·84	63·30	64·79	63·41	60·08	74·17
Al_2O_3 ..	10·20	21·07	18·14	17·81	12·38	17·16
Fe_2O_3 ..	5·41	2·41	1·50	3·26	3·28	7·82
FeO ..	7·48	4·25	5·90	5·97	4·20	..
MnO ..	..	0·10	0·36	0·09	0·18	..
MgO ..	1·96	1·79	1·33	1·94	1·95	0·83
CaO ..	1·10	1·24	1·07	1·13	9·43	0·61
Na_2O ..	1·95	1·88	2·33	1·86	2·59	0·49
K_2O ..	3·76	3·72	2·92	3·81	3·06	..
TiO_2 ..	..	0·16	0·89	0·25	0·65	..
H_2O^+ ..	0·05	0·20	0·65	0·22	1·80	0·11
H_2O^- ..	0·10	0·18	0·02	0·05	0·22	
Others ..	..	..	0·13	0·19	0·78	..
	99·85	100·30	100·3	99·99	100·60	101·79
si ..	274·5	244·5	266·7	240·8	195·1	405·2
al ..	24·3	48·0	44·0	30·0	23·6	55·0
fm ..	53·6	31·3	34·3	39·4	29·2	38·7
c ..	4·9	5·0	4·7	4·6	32·8	3·6
alk ..	17·2	16·0	17·0	16·0	14·4	2·7
ti ..	..	0·5	2·7	..	1·5	..
k ..	0·56	0·57	0·45	0·58	0·43	..
mg ..	0·22	0·33	0·28	0·36	0·45	..

AA : Garnetiferous gneiss, from near Sankellagummi, Pachipenta Zamindari, Analyst: G. G. K. Sastri.

AB : Bezwada gneiss, from the quarry adjoining Bezwada-Ellore Road and half a mile east of the town, Analyst : M. S. Rao (From thesis submitted to the Andhra University for M.Sc.).

AC : Khondalite, from Passara, Ceylon, Analyst : E. G. Radley, Adams, *Canadian Journal of Research*, Vol. I, p. 489.

AD : Khondalite, from the road between Kandy and Alunimuwara, Ceylon, Analyst : R. J. C. Fabry, *ibid.*

AE : Khondalite, from the road between Banderwala and Nuwara Eliya m.p.i., Ceylon, Analyst : M. S. Krishnan, *Rec. G.S.I.*, Vol. 48, p. 395.

AF : Khondalite, from Kalahandi State, Analyst : T. L. Walker, *Mem. G.S.I.*, Vol. 33, Part 3, p. 9.

The mode of the rock determined micrometrically is as follows:

Quartz	.. ..	44·58%
Felspar	.. ..	33·97%
Garnet	.. ..	18·36%
Biotite	.. ..	3·09%

The basis composition of the rock is given in Table II.

TABLE II

Kp	..	14·01
Ne	..	10·85
Cal	..	3·50
Sp	..	1·58
Fo	..	1·58
Fa	..	9·10
Fs	..	5·95
Q	..	51·51
		100·00

The normative compositions of the rock are given in Table III below:

TABLE III

	C.I.P.W. Norm.	Kata-Molecular Norm.
Q ..	36·19	31·05
Or ..	21·20	23·35
Ab ..	16·44	18·09
An ..	5·30	5·84
Hyp ..	15·78	8·17
En ..	..	4·67
C ..	0·58	..
Cord ..	..	2·88
Mt ..	4·51	5·95

Some discrepancies between the mode and norm are apparent. While there is about 43% normative felspar, the mode shows only 34%. The remainder may have gone partly into the constitution of mica and partly into garnet. No trace exists in the mode of the normative hypersthene and enstatite. They too might have gone into the constitution of the complex garnet. The corundum of the C.I.P.W. Norm is obviously represented by mica in mode.

Cordierite-Sillimanite-Garnet-Gneiss.—This is a medium grained and compact rock with the gneissosity clearly brought out, under the microscope, by the alternation of bands of quartz, felspar and cordierite with those of garnet, sillimanite and hypersthene. Magnetite is an abundant accessory.

Cordierite-Sillimanite Gneiss.—This rock is coarse grained and fresh and is made up of quartz, cordierite, sillimanite and hypersthene. Quartz and cordierite form a matrix in which are scattered nests of the other minerals. Cordierite also occurs as lenses and pockets in the rock.

Type B

Diopside-quartzite.—This rock is very fine-grained, compact and green in colour. Under the microscope it shows a mosaic structure typical of quartzites. The diopside is in small granules scattered through a matrix of recrystallised quartz.

A specimen with a specific gravity of 2·88 was chemically analysed. The results are given in Table IV below:

TABLE IV

Analysis of diopside-quartzite

	B
SiO_2 ..	83·58
Al_2O_3 ..	0·57
Fe_2O_3 ..	..
FeO ..	..
MgO ..	6·67
CaO ..	9·93
H_2O ..	0·10
	100·85
si ..	4·11
al ..	1·6
fm ..	49·2
c ..	49·2
alk ..	..
k ..	..
mg ..	1·0

B : Diopside quartzite from Lingalametta, Pachipenta Zamindari, Analyst : G. G. K. Sastri

The mode of the rock is given below:

Quartz..	..	60·33%
Diopside	..	39·67%

The basis composition of the rock is given in Table V.

TABLE V

Cal	..	0·85
Cs	..	13·99
Fo	..	14·45
Q	..	70·71

The normative composition of the rock is given in Table VI.

TABLE VI

	C.I.P.W. Norm.	Kata-molecular Norm.
Q ..	60·87	60·67
Di ..	37·42	..
En ..	..	19·27
Hyp ..	0·57	..
Wo ..	..	18·65
An ..	1·14	1·41

A comparative study of the mode and norm bring out some striking dissimilarities. The mode comprises mainly of quartz and diopside while the norm shows anorthite, hypersthene, enstatite and wollastonite. The presence of anorthite in the norm seems to point to the slightly aluminous nature of the diopside.

Type C

Biotite gneiss.—It is a medium grained leucocratic rock consisting of quartz, felspar, biotite and garnet. It exhibits gneissic banding and is much weathered. Under the microscope a little magnetite is seen in addition to the minerals above mentioned.

Chemical analysis of a more or less fresh specimen yielded the results given in Table VII.

TABLE VII

Analysis of biotite gneiss

	C
SiO_2 ..	89·74
Al_2O_3 ..	4·94
Fe_2O_3 ..	1·32
FeO ..	2·74
MgO ..	1·59
CaO ..	0·46
Na_2O ..	0·53
K_2O ..	1·26
H_2O ..	0·44
	100·02
sl ..	8·50
al ..	27·9
fm ..	54·6
c ..	4·7
alk ..	12·8
k ..	0·59
mg ..	0·12

C: Biotite gneiss from △ 1379, Pachipenta Zamindari, Analyst: G. G. K. Sastri

The basis composition is given below:

Kp	..	4·49
Ne	..	3·11
Cal	..	1·38
Sp	..	3·11
Fo	..	1·90
Fa	..	3·28
Fs	..	2·38
Q	..	81·35

The normative mineral composition is given in Table VIII.

TABLE VIII

	C.I.P.W. Norm.	Kata-Molecular Norm.
Q ..	76·60	71·95
Or ..	6·49	7·49
Ab ..	4·43	5·19
An ..	1·97	2·30
C ..	01·1	..
Cord ..	..	5·71
Hyp ..	8·61	3·45
En ..	..	2·53
Mt ..	0·98	1·28

Some normative minerals are absent in the rock. The hypersthene and enstatite of the norm appear to be represented by garnet, to the formation of which some anorthite may also have contributed. The corundum in the norm is obviously represented by mica in the rock.

Garnetiferous mica schist.—This is a dark brownish or black fissile consisting of a large proportion of biotite and subordinate garnet. Garnet occurs as idioblasts of pale-pink colour traversed by numerous cracks. The flakes of biotite are broken and irregular.

Crystalline limestone.—This is coarse-grained and white in colour. Small grains of diopside are scattered through the rock made up of crystals of calcite. The grains of calcite are seen under the microscope to be interlocked.

Type D

Augite Norite.—This is an even-grained melanocratic rock with a specific gravity of 3·09. Under the microscope it is seen to consist of plagioclase, hypersthene, augite, magnetite and a little free quartz. No potash felspar is seen. Magnetite, often titaniferous, is fairly abundant.

The results of the chemical analysis of this rock are given in Table IX.

TABLE IX

Analysis of Norite and Alkali Rocks

	DA	DB	DC	DD	DE	DF
SiO_2 ..	52·16	50·28	53·20	53·05	50·09	53·82
Al_2O_3 ..	17·56	18·08	12·53	8·91	16·52	8·07
Fe_2O_3 ..	2·01	2·10	3·29	3·26	1·97	2·11
FeO ..	9·31	9·28	14·17	9·52	11·45	7·01
MnO ..	..	0·36	0·12	0·09	0·45	0·21
MgO ..	7·39	7·02	1·08	14·42	5·88	18·39
CaO ..	7·01	9·34	6·58	6·76	9·03	5·96
Na_2O ..	2·44	2·38	2·73	0·66	2·64	1·28
K_2O ..	0·44	0·53	2·37	0·48	0·51	0·82
TiO_2 ..	1·04	0·80	1·91	1·77	1·49	0·33
P_2O_5 ..	..	0·30	0·16	0·09	0·35	0·04
H_2O^+ }	0·26	0·08	1·68	0·65	..	1·59
H_2O^- } ..		0·03	..		0·06	0·08
Others ..	..	..	..	..	..	0·05
	99·62	100·58	99·82	99·66	100·44	99·75
si ..	127·3	117·0	155·0	116·9	117·3	112·3
al ..	25·6	24·5	21·5	11·6	23·0	9·9
fm ..	49·7	46·5	46·0	70·4	48·0	73·1
c ..	18·3	23·0	20·5	15·9	23·0	13·3
alk ..	6·4	6·0	12·0	2·1	6·0	3·7
ti ..	1·9	1·5	..	..	..	..
k ..	0·09	0·12	0·30	0·32	0·30	0·30
mg ..	0·54	0·56	0·78	0·67	0·78	0·78

DA : Augite norite from Kagulageda, Pachipenta Zamindari, Analyst : G. G. K. Sastri.

DB : Norite, from Kondapalle, from quarries near road side, Ibrahimpatnam, Analyst : M. S. Rao (quoted from M.Sc. thesis).

DC : Upper norites Tanteshogte, Middleburg Dt., Analyst : J. Jacob, *Trans. Geol. Soc. of S. Afri.*, 35, 1932.

DD : Augite norite, from Eriyur, S. Arcot Dt., Analyst : P. Bruhl, *Rec. G.S.I.*, Vol. 30, p. 28, 1897.

DE : Augite norite, from St. Thomas Mount, Madras, Analyst : C. Rajagopalan (quoted from thesis submitted to B.H.U. for M.Sc.).

DF : Coarse norite, from the Central part of the dyke east of Durgapur, Keonjhar State, Analyst : P. C. Roy, *Rec. G.S.I.*, Vol. 71, p. 112.

Micrometric analysis of the rock gave the following percentages :

Quartz	5·25
Plagioclase ..	50·41
Pyroxene	37·74
Opaque ores	6·60

The basis composition is given in Table X.

TABLE X

Kp	..	1·35
Ne	..	13·12
Cal	..	21·03
Sp	..	1·18
Fo	..	14·97
Fa	..	10·88
Fs	..	2·19
Q	..	34·55
Ru	..	0·73

The normative mineral compositions are given in Table XI below:

TABLE XI

	C.I.P.W. Norm.	Kata-Molecular Norm.
Qr ..	4·70	2·74
O ..	2·06	2·25
Ab ..	20·10	21·86
An ..	32·22	35·05
Hyp ..	37·11	13·04
En ..	..	19·96
C ..	0·45	..
Cord ..	..	2·18
Mt ..	1·68	2·19
Il ..	1·68	..
Ru ..	..	0·73

A close resemblance between the mode and norm can easily be perceived. The normative orthoclase may be in solid solution with the plagioclase, for Winchell says that labradorite is capable of taking up as much as 6% of orthoclase into its constitution. There is a small amount of normative corundum which may have gone into the constitution of hypersthene. The anorthite content of the plagioclase is 60, a value which agrees closely with that obtained from optical data.

PETROCHEMICAL STUDIES ON THE GENESIS OF KHONDALITES

The chemical analyses of the three members of the Khondalite series, given above, yield some valuable information on the petrogenesis of the series. The well-known methods of Niggli and Osann are followed in this connection. It has been pointed out earlier that the field characters of these rocks are such as to suggest that they are metamorphosed sediments. This finds support from the following discussion on the petrochemistry of the rock types.

The al, alk, and c/fm values of the rocks are calculated as laid down by Niggli and tabulated below: (Table XII).

TABLE XII

	al	alk	c/fm
A ..	24·3	17·2	0·08
B ..	1·6	..	1·0
C ..	27·9	12·8	0·08

Taking the corresponding c/fm value, the values are plotted in the appropriate triangles. A and C (Fig. 1) fall in the field of argillaceous sediments but it can also be seen that they are not very rich in alumina

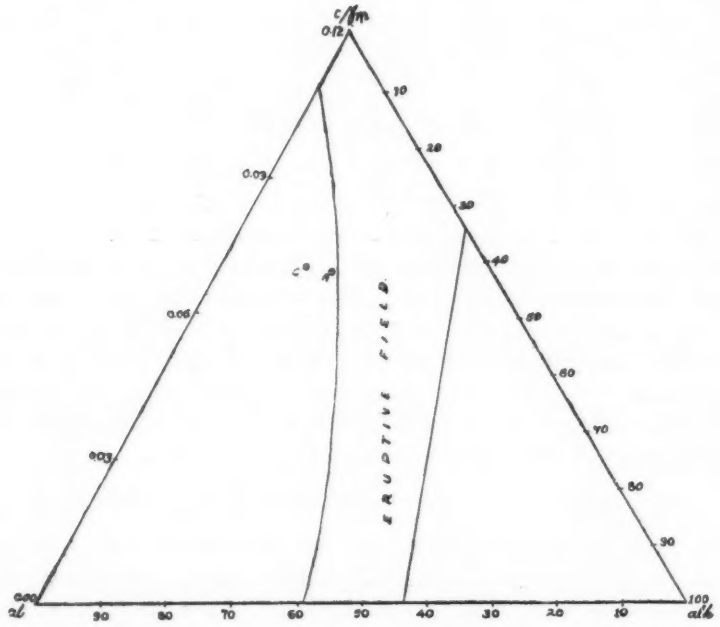


Fig. 1. *al-alk-c/fm* Diagram for the Metamorphics (Johannsen, 1939, p. 106)

B (Fig. 2) falls near the lime apex of the triangle and from the c/fm value, its original dolomitic nature can be made out.

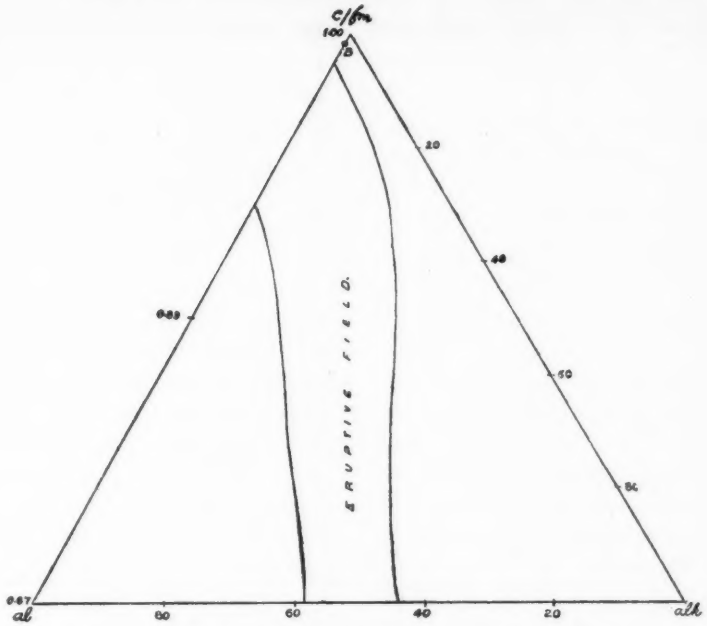


Fig. 2. *al-alk-c/fm* Diagram for Metamorphics (Johannesen, 1939, p. 106)

The S, Al and F values as well as the C, Al and Alk values of the rocks are calculated according to Osann. They are given in Table XIII below:

TABLE XIII

	S	Al	F	Al	C	Alk
A ..	23	2	5	16	3	11
B ..	24	0	6	1	29	0
C ..	27	1	2	18	3	9

In Fig. 3, the S, Al and F values are plotted in the corresponding diagram and it can be seen that all the points fall outside the eruptive field. The same result is seen (Fig. 4), where the Al, C and Alk values of the rocks are plotted in the corresponding trilinear diagram. Thus it can be definitely seen that the three rock types are metamorphosed representatives of original sediments.

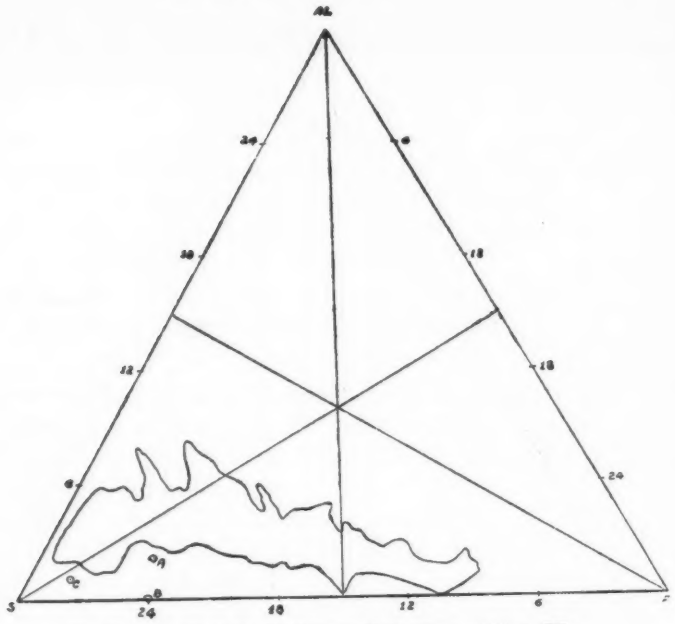


Fig. 3. Osann's S-AL-F Diagram (Johannsen, 1939, p. 79)

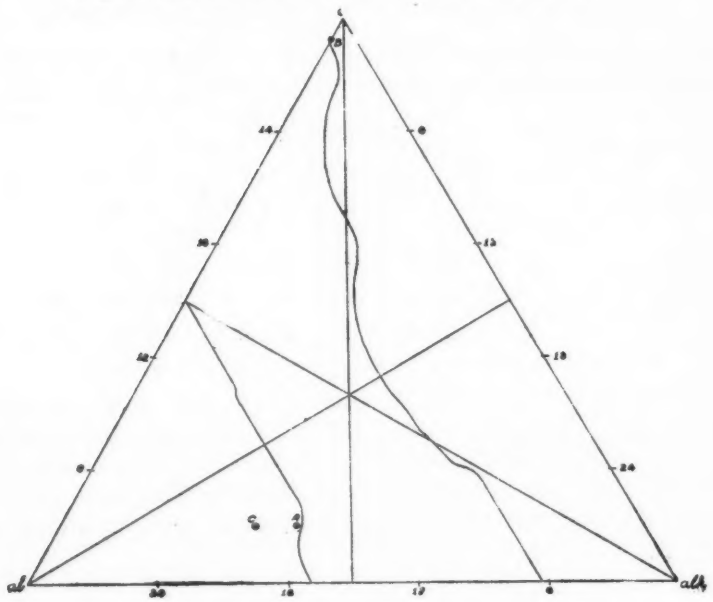


Fig. 4. Osann's *c-al-alk* Diagram (Johannsen, 1939, p. 79)

Further evidence in the same direction is furnished by the following general observations on the chemical composition of the rocks, which are characteristic of sediments.

The rocks are characterised by—

(i) an excess of silica figuring to a great extent as normative quartz,
(ii) an excess of alumina, figuring as normative corundum,
(iii) a preponderance of potash over soda, and
(iv) a slight excess of magnesia over lime, if not in equal proportions.

The original sediment that on metamorphism, gave rise to the garnetiferous gneiss must have been more siliceous and less aluminous than a normal argillaceous sediment. The poverty of the sediment in alumina is reflected in the absence of sillimanite in the rock.

The metamorphism of an argillaceous sandstone seems to have given rise, in a more or less high grade, to the biotite gneiss. The high silica content bears ample testimony to this view.

An arenaceous sediment with dolomitic impurities is apparently the parent rock of the diopside quartzite. Diopside is the most appropriate silicate in the conditions specified as it takes up the maximum amount of silica for a given lime and magnesia content and thus can occur to the exclusion of other silicates.

No definite view can be expressed on the nature of the metamorphism that gave rise to the series. The mosaic structure of the diopside quartzite and the absence of intense granulation seem to point to the metamorphism being thermal rather than regional.

Petrogenesis of the khondalites.—Close agreement exists between several geologists like Walker, Middlemiss and Crookshank on the question of the origin of khondalites. They all regard the khondalites as the metamorphosed representatives of original sediments of varying composition. Since the series in the area consists of such members as biotite schists, crystalline limestones, diopside quartzites, sillimanite- and graphite-gneisses, the above view finds support here. No evidences, it is to be pointed out in conclusion, have been found to postulate a later felspathisation of the series.

Petrochemical Study of the Charnockites

A comparative study of the chemical analyses listed in Table IX will make the close similarity between the norites of the area and those of Pallavaram and Kondapalli apparent. Field characteristics seem to point to an igneous intrusive origin for the augite norites of the area. Much information could not be obtained on the trends of differentiation since only norites are exposed here.

An attempt is made, however, to ascertain the affinities of this rock type with one of the three petrographic provinces—Pacific, Atlantic and Mediterranean. The Q, L, M, K and π values of the rock are given in Table XIV below along with the corresponding values for the Bushveld norites, to bring out the close similarity that exists between them.

TABLE XIV

		Q	L	M	K	π
Norite	(Bhushveld)	35·2	36·0	28·8	0·05	0·73
Norite		32·5	34·8	32·7	0·08	0·68
Norite		30·8	35·2	34·0	0·08	0·58
Norite		32·4	34·2	33·4	0·13	0·67
Norite	(Pachipenta)	34·6	35·5	29·9	0·09	0·59

In Fig. 5, the K, π values of the rock are plotted. The point can be seen to fall well within the field of Pacific suite indicating its affinity with the calc-alkaline series.

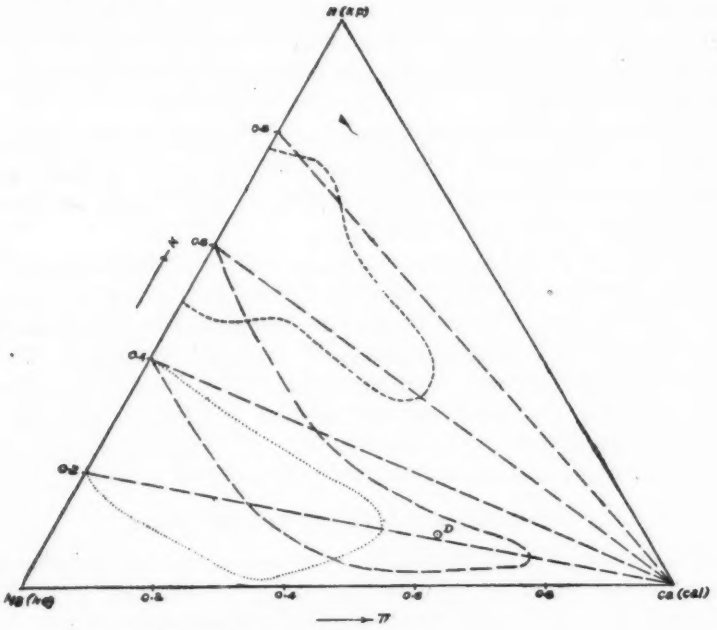


Fig. 5. Kπ Diagram for the charnockites.

— — — — Pacific
- - - - - - - - - Mediterranean
. . . . . Atlantic

Petrogenesis of the charnockites.—The literature on this subject is so vast that no attempt is made to enumerate the various views expressed by the many workers connected with the study of charnockites in India and elsewhere. On one side Holland (1900) regarded the charnockite series as of magmatic origin and constituting a petrographic province. On the other, B. Ramarao (1945) goes to the extent of calling the series a metamorphic province, the various members having resulted from " repeated metamorphism of a composite series of ancient impure sediments " with the phenomenon of assimilation playing an important part. As has already been pointed out the study of charnockites from the area is limited in scope and the available field and laboratory data seem to point to an igneous intrusive origin.

Economic Geology

Old workings for graphite and mica are found in the area, besides some outcrops of rocks bearing these and other minerals in good quantities. A brief description of the individual occurrences is given below:

Mica.—Ruby muscovite of fine quality occurs in the pegmatites intruding the biotite gneisses and mica-schists. Two outcrops are worth describing.

(*a*) On the Western flanks of Δ 1379, at Yerravadlavalasa, is an exposure of pegmatites trending in a North-South direction. The country rocks have a strike of N.W.-S.E., and dip at 60° towards S.W. The exposure is 25 ft. by 15 ft. and is surrounded by thick forest. Mica books of fair quality and measuring 4" in width occur without any fixed orientation in the pegmatites. Similar pegmatitic material is also exposed further north and south of this outcrop.

(*b*) Biotite gneisses intruded by mica-bearing pegmatites are exposed in the lower levels of the Kagulageda hill near the foot-path leading from Bodanayudu-Valasa to Kagulageda. This outcrop differs from the previous one in the smaller width of the individual pegmatite which is 2 ft.

Considering the industrial importance of fine ruby mica, and in view of the fact that mica occurs in pegmatites in concentrated books along the vein, it may be worth while to undertake the risk of preliminary mining upto a depth of 60'–80' to prove these deposits.

Old workings for mica are found near the foot of the Padmapuram hill. The mica that was mined here is decidedly superior to that from any of the above localities both in size and quality. Careful prospecting by trial pits may lead to the location of some rich pegmatites.

Graphite.—The occurrence of graphite in the crystalline rocks of Vizagapatam District was first recorded by King. Admitting that the

mineral is not known to occur in quantity, he suggests that neighbourhood of Salur may prove a good locality.

In the area, graphite occurs on Sudikonda near Alluru. The country rocks are biotite gneisses which contain graphite in isolated patches. No quartz veins or pegmatites are exposed in the vicinity. Analysis has shown that the mineral makes up about 10% of the rock. Since graphite occurring in the nearby localities in workable quantities is associated with rocks similar to the ones exposed here and since methods are being perfected for concentrating low grade graphite ores into high grade ones at a low cost, it may prove economically feasible to work these deposits in the near future.

In view of its uniform mode of occurrence in these paragneisses, the author feels that it is a primary constituent of these rocks and represents the metamorphosed carbon impurity of the original sediments.

Old workings for graphite exists on Lingalametta. Graphite is said to occur in good lumps to find a ready market. Mining seems to have proceeded to depths of 50′ to 60′, but the pits are all covered up. The presence of bands of crystalline limestone and a few pegmatites in the vicinity are encouraging.

Earthy limestone.—A layer of earthy limestone or calctufa occurs in the soil to the North of Pachipenta. It is 1′ to 1½′ thick and is situated at a depth of 10′ from the surface. It is fairly extensive and is being mined and calcined for lime.

Ilmenite occurs on △1379, in association with magnetite. The extent of the deposits is uncertain.

Crystalline limestone.—The occurrence of bands of crystalline limestone on Lingalametta has already been mentioned. If non-magnesian, they may support a small-scale bleaching powder industry.

Summary and Conclusions

In this paper, the results of field and laboratory study on the geology, petrochemistry, petrogenesis and economics of the Pachipenta Zamindari have been presented.

A succession of the various members of the khondalite series has been given. Based on petrochemical evidence, the biotite gneiss is considered to represent a metamorphosed argillaceous sandstone. The parent rock of the garnetiferous gneiss is considered to be an argillaceous sediment somewhat poor in alumina. The diopside quartzite has been considered to be the metamorphosed representative of a dolomitic sandstone. Petrographic descriptions of the other members of the khondalite series have been given,

Petrochemical study of the charnockites has also been made and the striking resemblance of the augite norites of the area to the norites of Bushveld has been pointed out as also its general affinities with the calc-alkaline suite of igneous rocks. An igneous intrusive origin has been attributed to these rocks. A brief description of the economics of the area has also been given.

ACKNOWLEDGMENTS

The work was carried out in the laboratories of the Geology Department of the Andhra University at Waltair. The author has great pleasure in placing on record his heartfelt gratitude to Prof. C. Mahadevan, M.A., D.Sc., for having suggested the problem, his guidance and the keen interest he evinced in the progress of the work. He thanks Mr. M. Venkatarao of Kovvur for affording facilities in the field.

BIBLIOGRAPHY

Benza, P. M. .. "Notes chiefly geological of a journey through the Northern Circars in the year 1835," *Mad. Jour. Lit. Sci.*, 1897, **5.**

Carmichael .. *A Manual of Vizagapatam District*, 1869.

Crookshank, H. .. "The Western Margin of the Eastern Ghats," *Rec. G.S.I.*, 1938, **43**, 398–424.

Fermor, L. L. .. "An attempt at the correlation of the Ancient Schistose formations of Peninsular India," *Mem. G.S.I.*, 1935, **70**, Parts 1 and 2.

Hess, H. H., and Phillips, F. H. "Orthopyroxenes of the Bushveld type," *Amer. Min.*, 1938, **23**, 400–56.

Holland, T. H. .. "The Charnockite series, a group of Archæan Hypersthenic rocks in Peninsular India," *Mem. G.S.I.*, 1900, **28**, Part 2.

Johannsen, A. .. *A Descriptive Petrography of Igneous Rocks*, 1939.

King, W. .. "Geological Sketch of the Vizagapatam Dist.," *Rec. G.S.I.*, 1886, **19**, Part 3.

Lacroix .. "Gneissose Rocks of Salem," *ibid.*, 1891, **24**, Part 3, 155–200.

Mahadevan, C. .. "Geology of the Vizagapatam Harbour area," *Quart. Journ. Geol. Min. Met. Soc. Ind.*, 1929, **2**, No. 4.

Mahadevan, C., and Gopalakrishna Sastry, G. Optically Positive Cordierite from the Khondalites of Pachipenta, *Proc. Ind. Acad. Sci.*, 1948, A, **27**, 361–365.

Middlemiss, C. S. .. "Note on a sapphirine bearing rock from Vizagapatam Dist.," *Rec. G.S.I.*, 1904, **31**, Part 1, 38–42.

Rama Rao, B. .. "The Charnockite Rocks of Mysore," *M.G.D. Bull.*, 1945, 18.

Sen Gupta, K. K. .. "On the Hypersthenisation of Monoclinic Pyroxene (in Charnockite)," *Jour. As. Soc. Beng.*, 1916, N.S. **12.**

Smith, F. H. .. "Preliminary Report of the Geology of Ganjam Dist.," *G.S.I. Gen. Rep.*, 1899–1900, 1900, cxxi.

Walker, T. L. .. "The Geology of the Kalahandi State," *Mem. G.S.I.*, 1902, **33**, Part 3.

,, and Collins, W. H. .. "Petrological study of some rocks from the Hill tracts, Vizagapatam Dist.," *Rec. G.S.I.*, 1907, **36**, 1–18.

Washington, H. S. .. "The Charnockite series of Igneous rocks," *Amer. Jour. of Sci.*, 1916, **41**, Art. XXII, 323.

Winchell, A. N. .. *Elements of Optical Mineralogy*, 1927.

CONDENSATION OF ALDEHYDES WITH AMIDES

Part XVII. Of 5-Chloro- and 3: 5-Dichlorosalicylaldehydes

By Ram Ghulam Singh Nigam and Kantilal C. Pandya

(*Chemistry Laboratory, St. John's College, Agra*)

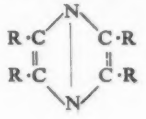
Received January 6, 1948

In Part I of this series[7] have been described studies on the condensations of several amides with salicylaldehyde under different conditions. It has been shown that under all the conditions examined only one product was formed, namely, salicylidene-monoamide, and that, of all these conditions, the one using $\frac{1}{8}$th of a molecule of pyridine at water-bath temperature gave the highest yield, which at times was nearly quantitative. Later work showed that condensations with *m*-hydroxy-[10] and *p*-hydroxy-[11] benzaldehydes gave also similar -monoamide products, but when there were groups on the aromatic ring like methyl,[9, 15] methoxy,[12] methylenedioxy,[13] nitro,[14] chloro,[16] $-CH:CH.CHO$,[8] $-CH_2CH_2.CHO$[17] and so on, the product was invariably the *-bis*amide type. Benzaldehyde[16] and *n*-heptaldehyde[18] also gave *-bis*-amides. It has also been found that in most of these cases the presence of pyridine was not always favourable; in some cases it led to resinification; higher yields came out generally when the aldehyde and the amide were heated alone, preferably, in some cases, at 100–110°.

The condensations of two different chloro-derivatives of salicylaldehyde, 5-chloro- and 3: 5-di-chloro-salicylaldehydes, with about eight amides, under two or three different conditions, are described here. They present a good contrast with those of salicylaldehyde itself.[7]

The monochloro- derivative gave *-mono*amides but only with three amides, with *n*-heptamide, with benzamide and with benzene-sulphonamide, and gave *-bis*amides with all the others including benzamide also, which last thus gave both the products. In the case of the dichlorosalicylaldehyde, it gave the *bis*-products with all except with benzene-sulphonamide. Urea gave the two usual products according as the condensation was carried out above or below the melting-point of urea.[4] Formamide was peculiar as it often has been found to be; it gave corresponding pyrazine-derivatives*

* Bülow[3] has earlier established the formation of tetraphenylpyrazine from the condensation at high temperatures of benzaldehyde with formamide[16]; a related product has also been obtained in this laboratory from the condensation of cinnamaldehyde with formamide.[1]



[R = C_6H_5 (Bülow[3]); and = C_6H_3 (OH) Cl and = C_6H_3 (OH) Cl_2 in the present paper]

(tetra-monochloro-hydroxyphenyl-pyrazine and tetra-dichlorohydroxyphenyl-pyrazine) in both cases, but with a little of the -*bis*formamide also in the case of the 3: 5-dichlorosalicylaldehyde.

There was also considerable disparity in the yields. Excepting in two cases, in the condensations with formamide and with urea, the yields obtained from the condensations of the dichlorosalicylaldehyde were all higher, sometimes very much higher, than those obtained from the condensations of the monochlorosalicylaldehyde; in two cases (propionamide- and benzenesulphonamide-dichloro-salicyl aldehyde condensations) the yields were very nearly theoretical.

The mono- and the bis-amides were distinguished not only by analysis but also by the usual properties associated with each of the derivatives, particularly by the reactions with Baeyer's reagent and the coloration with cold concentrated sulphuric acid.

Urea has been found to give very useful and important condensation-products by reacting with aldehydes and the products often differ according to different conditions. (See also Das Gupta.[4]) Urea has thus been included in the list of the amides tried in these condensations. It has been condensed with *n*-heptaldehyde (Pandya and Sodhi, H. S.[18]) and also with the two chloro-salicylaldehydes included in the present paper. The yields here have not been high.

Similarly benzenesulphonamide presents another type of an amide, having an $-SO_2NH_2$ group instead of the $-CONH_2$ group. Earlier workers in this Laboratory (notably George[5]) failed to obtain a condensation-product from it with some aldehydes. We, however succeeded in obtaining mono-amide products, in one case in theoretical yields, from the two aldehydes considered in this paper. Later another worker (Mhala[6]) also succeeded in condensing it with another aldehyde (3: 5-dibromo-salicylaldehyde).

Experimental

Preparation of the Chloro-salicylaldehydes

5-*Chlorosalicylaldehyde*.—Biltz and Stepf[2] prepared it by passing for one hour a stream of chlorine in salicylaldehyde kept on water-bath, and reported an yield of 66.7% and the melting-point 99.5°. We found that the room-temperature (23°) gave a better yield, 77.6%, and the final melting-point was 101°.

3: 5-*Dichlorosalicylaldehyde*.—Biltz and Stepf[2] prepared this by passing dry chlorine for one hour into a glacial acetic acid solution of salicylaldehyde kept on waterbath. While they reported an yield of 90%, only a 58% yield

was obtained by us: but by changing the proportion of glacial acetic acid solution, from 1 : 5 to 1 : 3.2 grams, it was found that the yield rose to 85%: the melting-point was identical, 95°.

Condensations with Acetamide

5-*Chlorosalicylaldehyde* (0.8 gr.) and acetamide (0.6 gr.), (1 : 2 mol.), were heated alone on water-bath (98°) for eight hours. The pale yellow hard solid with a buff-coloured rim was washed with hot water and then with ether: it gave a crude product that melted at 208°, and, after recrystallisation from alcohol, melted finally at 227°. It came out then in white crystalline needles. Cl, found 13.61%: monochlorosalicylidene*bis*acetamide $C_{11}H_{13}O_3N_2Cl$ requires 13.84%, and monochlorosalicylidene*mono*acetamide $C_9H_8O_2NCl$ requires 17.97%. The yield here was 45.75% of theory. Heating at 100–110° gave a 53% yield.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and acetamide (0.6 gr. : 1 : 2 mol.) were heated in the same way. Within ten minutes the mass fused to a clear liquid and crystals began to be formed in 45 minutes, after which the whole began to set to a hard yellow mass. After the usual treatment the crude product melted at 199°, and, after recrystallisation (warm alcohol), finally at 204.5°. Cl, found 24.25%: dichlorosalicylidene*bis*acetamide $C_{11}H_{12}O_3N_2Cl_2$ requires 24.39%, dichlorosalicylidene*mono*acetamide $C_9H_7O_2NCl_2$ requires 30.6%. The yield was 46.46%.

In the presence of pyridine (1 : 2 : 0.15 mol.) the yield decreased to 20%, but when the heating was carried on at 100–110°, in the absence of a condensing agent, the yield increased to 86.28%.

Condensations with Propionamide

5-*Chlorosalicylaldehyde* (0.8 gr.) and propionamide (0.75 gr., 1 : 2 mol.) were heated on water-bath as above. The product, recrystallised from alcohol, melted at 188°. Cl, found 12.35%: monochlorosalicylidene*bis*propionamide $C_{13}H_{17}O_3N_2Cl$ requires 12.47%, while the monochlorosalicylidene*mono*propionamide $C_{10}H_{10}.O_2NCl$ requires 16.78%. The yield was 35% of theory, but it increased to 44% when the condensation was carried out at 100–110°.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and propionamide (0.75 gr., 1 : 2 mol.) were heated on water-bath in the same way. White needle crystals, recrystallised from alcohol, melted at 195.5° and regenerated the aldehyde and the amide when heated with mineral acids. Cl, found 22.11%: dichlorosalicylidene*bis*propionamide $C_{13}H_{16}O_3N_2Cl_2$ requires 22.26%, while the dichlorosalicylidene*mono*propionamide $C_{10}H_9O_2NCl_2$ requires 28.86%.

The yield was 65.8% of theory. When the same condensation was carried out by heating for 24 hours in the presence of pyridine acetate (1 : 2 : 0.15 mol.), the yield was 48.6%, and in the presence of pyridine, 68.4%. But on heating without any condensing agent at 100–110°, the yield became nearly quantitative (99.6%).

Condensation with n-*Butyramide*

5-*Chlorosalicylaldehyde* (0.8 gr.) and *n*-butyramide (0.9 gr., 1 : 2 mol.) were heated as usual on water-bath, and gave a product melting at 166° after several recrystallisations from alcohol. Cl, found 11.58%: monochlorosalicylidene*bis*-butyramide $C_{15}H_{21}O_3N_2Cl$ requires 11.36%, while monochlorosalicylidene*mono*butyramide $C_{11}H_{12}O_2NCl$ requires 15.75%. The yield is 73.27% of theory: a higher temperature gave a lesser yield 40%.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and *n*-butyramide (0.87 gr., 1 : 2 mol.), when heated as usual on water-bath, gave a milk-white product melting at 175–177°, and at 179° after recrystallisation from alcohol. Cl, found 20.84%: dichlorosalicylidene*bis*butyramide $C_{15}H_{20}O_3N_2Cl_2$ requires 20.46%, while dichlorosalicylidene*mono*butyramide requires 27.31%. The yield was about 53%, but increased to 85% of theory when the heating during the condensation was 100–110°.

Condensations with n-*Heptamide*

5-*Chlorosalicylaldehyde* (0.8 gr.) and *n*-heptamide (1.3 gr., 1 : 2 mol.), when heated alone on water-bath, gave no solid product even after six hours. The temperature was gradually raised to 140–150°, when solidification took place. Washing with water and with petroleum ether (b.p. 55–70°) gave a lemon-yellow solid almost insoluble in the ordinary organic solvents. After frequent washings with hot alcohol it decomposed at 268°. Cl, found: 13.19%: monochlorosalicylidene*bis*heptamide $C_{21}H_{23}O_3N_2Cl$ requires 8.95%, while monochlorosalicylidene*mono*heptamide $C_{14}H_{18}O_2NCl$ requires 13.27%. The monoheptamide decolorised Baeyer's reagent rather slowly and gave a deep red colour with concentrated sulphuric acid. The yield was only 18.6%.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and *n*-heptamide (1.3 gr., 1 : 2 mol.), heated on water-bath as usual, gave a product melting at 144°, or at 147° after recrystallisation (alcohol). Cl, found: 16.21%: dichlorosalicylidene*bis*heptamide $C_{21}H_{32}O_3N_2Cl_2$ requires 16.47%, while dichlorosalicylidene*mono*heptamide requires 23.51%. The yield was 46% of theory but increased to 79% when the heating was at 100–110°.

Condensation with Benzamide

5-*Chlorosalicylaldehyde* (0.8 gr.), benzamide (1.2 gr.) and pyridine acetate (1 : 2 : 0.15 mol.) were heated on waterbath for 24 hours, after which by the usual procedure a product melting at 194°, after a recrystallisation from 90% alcohol, was separated. Cl, found : 9.81% : monochlorosalicylidene-*bis*benzamide $C_{21}H_{17}O_3N_2Cl$ requires 9.32%, while monochlorosalicylidene-*mono*benzamide $C_{14}H_{10}O_2NCl$ requires 13.68%. The yield was 46.26% of theory. It decolorised Baeyer's reagent but gave no colour with cold concentrated sulphuric acid.

A second experiment under the same circumstances, except that the heating was for 48 hours, gave 56.54% yield.

A third experiment of heating the aldehyde and the amide alone at 150–160° for eight hours gave a different product. It was a hard solid and after repeated washings with ether, hot alcohol and petroleum ether (b.p. 55–75°), it decomposed at 269° without melting. Cl, found : 13.98%, corresponding to the monochlorosalicylene*mono*benzamide which requires 13.68% (*vide* above). The yield was 40.7% and the product might have been a polymer. It decolorised Baeyer's reagent and also gave a deep red colour with cold concentrated sulphuric acid.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.), benzamide (1.2 gr.) and pyridine (1 : 2 : 0.15 mol.) were heated for 8 hours on water-bath. The hard yellow cake, after purification, melted at 202°. Cl, found : 17.47% : dichlorosalicylidene*bis*benzamide $C_{21}H_{16}O_3N_2Cl_2$ requires 17.10%, while dichlorosalicylidene-*mono*benzamide $C_{14}H_9O_2NCl_2$ requires 24.15%. The yield was 28.46% but increase to 47.43% when the two were heated without pyridine, and to 85.7% when, without pyridine, the temperature of the bath was 100–110°.

Condensations with Benzenesulphonamide

5-*Chlorosalicylaldehyde* (0.2 gr.) and benzenesulphonamide (0.4 gr., 1 : 2 mol.) were heated for 8 hours at 140–150° (there being no reaction below this). The product melted at 170°, the melting-point remaining unchanged on recrystallisation (hot alcohol). Cl, found : 11.99% : chlorosalicylidene-*bis*benzenesulphonamide $C_{19}H_{17}O_5S_2N_2Cl$ requires 7.4%, while the chlorosalicylidene*mono*benzenesulphonamide $C_{13}H_{10}O_3SNCl$ requires 12.01%. The yield of the monoamide was 37.4%, which increased to 60% when the condensation was carried out at 150–160°. The product was soluble in alcohol, benzene, acetone and chloroform; it decolorised immediately Baeyer's reagent and gave a deep red colour with cold concentrated sulphuric acid.

3 : 5-*Dichlorosalicylaldehyde* (0.25 gr.) and benzenesulphonamide (0.4 gr., 1 : 2 mol.) were heated at 120–130° for 8 hours and gave, after a recrystallisation from cold alcohol, a white product melting at 196°. Warming with even rectified spirit decomposed it back into the original aldehyde and the amide. It decolorised neither Baeyer's reagent nor bromine water. S, found: 9.96%: Cl, found: 21.71%: dichlorosalicylidene*bis*benzenesulphonamide $C_{19}H_{16}O_5N_2S_2Cl_2$ requires 13.14% and 14.58% respectively, while dichlorosalicylidene*mono*benzenesulphonamide $C_{13}H_9O_3NSCl_2$ requires 9.69 and 21.51% respectively. The yield of the monoamide was 37.5%, and rose to 61.9%, when the heating was at 130–140°, for five hours: at 140–150°, the reaction took only four hours and the yield was nearly theoretical.

Condensations with Urea

5-*Chlorosalicylaldehyde* (0.8 gr.), urea (0.6 gr.) and pyridine (1 : 2 : 0.15 mol.) were heated at 140–150° for seven hours when a deep orange-coloured liquid was obtained. It solidified overnight and was washed respectively with water, dilute hydrochloric acid and ether. Recrystallisation (twice from alcohol) gave a yellow product melting at 241° (dec.). Cl, found: 14.27%: chlorosalicylidenebiuret $C_9H_8O_3N_3Cl$ requires 14.69%. The yield was 44.5%.

When the same experiment was repeated at a temperature below the melting-point of urea, at 120–125°, a different product was obtained melting at 226°. The same product came out also in the presence of pyridine, but the yield in both cases was meagre. The yield was improved in the presence of 2 c.c. of 90% alcohol (on water-bath). The alcohol evaporated leaving behind an orange mass, which on purification melted at 226° (dec.). Cl, found: 13.34%; chlorosalicylidenediurea $C_9H_{12}O_3N_4Cl$ requires 13.69%. The yields were 37.8 and 27.7% respectively without and with pyridine.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and urea (0.6 gr.) were heated, in two separate flasks, with and without pyridine as before at 150–160° for seven hours, but charring took place in both. In another experiment a lower temperature (132–140°) was tried, which in seven hours gave a yellowish substance melting at 261°. It was insoluble in water or in ordinary organic solvents, but dissolved in alkalies from which it could be reprecipitated. Cl, found: 25.28%: dichlorosalicylidenebiuret $C_9H_7N_3O_3Cl_2$ requires 25.72%. The yields were 35.9 and 21.13% respectively.

The same experiments when repeated on a water-bath gave a product melting at 175° with an orange colour and resembling the above in its general insolubility. It also decomposed into the original aldehyde and urea when

it was heated with mineral acids. Cl, found: 23.96%: dichlorosalicylidene-diurea $C_9H_{10}N_4O_3Cl_2$ requires 24.23%. The yields were poor but increased to 11.9 and 9.3%, when the heating was at 128–130°.

Condensations with Formamide

5-*Chlorosalicylaldehyde* (0.8 gr.) and formamide (0.45 gr., 1 : 2 mols.), heated on water-bath for 8 hours, gave, after the usual treatment and recrystallisation (hot alcohol), a yellow substance melting at 270°. Cl, found: 24.62%: monochlorosalicylidene-*mono*formamide $C_8H_6O_2NCl$ requires 19.34%, chlorosalicylidene-*bis*formamide $C_9H_9O_3N_2Cl$ requires 15.53%, and tetramonochlorosalicylpyrazine $C_{28}H_{16}N_2O_4Cl_4$ requires 24.23%. The yield was 80%. The product affected neither Baeyer's reagent nor cold concentrated sulphuric acid.

3 : 5-*Dichlorosalicylaldehyde* (1.0 gr.) and formamide (0.45 gr.) were heated at 100–105° for 8 hours, when an orange mass was obtained: it was left soaking in water for twenty-four hours when it changed into a yellow plastic. There was much resin, but it was resolved into two parts, one soluble, the other insoluble, in alcohol. The former, coming out in white needle crystals, melted at 207°. The latter melted at 227°. Cl, found in the first 26.91%; dichlorosalicylidene-*bis*formamide $C_9H_8O_3N_2Cl_2$ requires 26.99%, while dichlorosalicylidene*mono*formamide $C_8H_5O_2NCl_2$ requires 32.56%. Cl, found in the second was 39.01%; tetradichlorosalicylpyrazine $C_{28}H_{12}O_4N_2Cl_8$ requires 39.22%. The yield of the first was only 3.6% and that of the second was 10.5%. When the condensation was conducted at 120–130°, the former disappeared and the latter increased to 21.1%.

Summary

5-Chloro- and 3 : 5-dichlorosalicylaldehydes have been condensed with different amides under different conditions. In contrast with the *-mono-* amides obtained in all the salicylaldehyde-amide condensations,[7] the monochlorosalicylaldehyde gave monoamides with only three amides, of which one, benzamide, gave the bis- product as well. The 3 : 5-dichlorosalicylaldehyde gave the monoamide only once, in its condensation with benzenesulphonamide: for all the rest the -bis product was the usual rule. This may be one of the effects of the chlorine on the aromatic ring of the aldehyde. Except in one case the yields in the dichlorosalicylaldehyde-amides condensations were all higher than those of the monochloro-aldehyde-amide condensations, reaching, in condensations with propionamide and benzenesulphonamide, the quantitative limits. Usually the highest yields were obtained at 100–110° and in the absence of any condensing agent.

TABLE

Amides	Maximum yields with Salicylaldehyde[7]	5-Chlorosalicyl-aldehyde		3 : 5-Dichloro-salicylaldehyde	
Formamide ..	100 -mono-	0		10·5	-bis-
		80	-bis-	21·1	pyrazine derivs.
Acetamide ..	98 ,,	53	-bis-	86·28	-bis-
Propionamide ..	88·2 ,,	44	,,	99	,,
n-Butyramide ..	not tried	73	,,	85	,,
n-Heptamide ..	,,	18	-mono-	79·5	,,
Benzamide ..	96·4 -mono-	40	,,	85·7	,,
		56	-bis-		
Benzenesuphonamide ..	not tried	60	-mono-	100	-mono-
Urea ..	,,	44	diurea	11·3	diurea
		37·8	biuret	36	biuret

REFERENCES

1. Baslas, K. K. .. *M.Sc. Thesis*, 1942 (unpublished).
2. Biltz and Stepf .. *Ber.*, 1904, 4027.
3. Bülow .. *Ibid.*, 1893, 1972.
4. Das Gupta .. *Journ. Ind. Chem. Soc.*, 1933, **9**, 117.
5. George, J. .. *Thesis*, 1943 (unpublished).
6. Mhala, M. .. *Ibid.*, 1945 (unpublished).
7. Pandya and Sodhi, T. S. .. *Proc. Ind. Acad. Sci.*, 1938, **7**, 361.
8. ——— and Mehra .. *Ibid.*, 1938, **7**, 376.
   ——— and Bhandari .. *Journ. Ind. Chem. Soc.*, 1947, **24**, 209.
9. ——— and Mehra .. *Proc. Ind. Acad. Sci.*, 1939, **9**, 508.
10. ——————— ,, .. *Ibid.*, 1939, **10**, 279.
11. ——— and Mansur .. *Ibid.*, 1939, **10**, 282.
12. ——— and Mehra .. *Ibid.*, 1939, **10**, 285.
13. ——— and Varghese .. *Ibid.*, 1941, **14**, 18, 25.
14. ——— and Ittyerah .. *Ibid.*, 1942, **15**, 6, 252.
15. ———, Agrawal and Tripathi .. *Journ. Ind. Chem. Soc.*, 1944, **21**, 383.
16. ——— and Bhatnagar .. *Proc. Ind. Acad. Sci.*, 1946, **24**, 487.
17. ——— and Bhandari .. *Journ. Ind. Chem. Soc.*, 1947, **24**, 185.
18. ——— and Sodhi, H. S. .. *Proc. Ind. Acad. Sci.*, 1948, **27**, 196.

1188-48 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent
and Published by The Indian Academy of Sciences, Bangalore